Evaluated Kinetic, Photochemical and Heterogeneous Data for Atmospheric Chemistry: Supplement V

IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry

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This paper updates and extends previous critical evaluations of the kinetics and photochemistry of gas-phase chemical reactions of neutral species involved in atmospheric chemistry [J. Phys. Chem. Ref. Data **9**, 295 (1980); **11**, 327 (1982); **13**, 1259 (1984); **18**, 881 (1989); **21**, 1125 (1992)]. The work has been carried out by the authors under the auspices of the IUPAC Subcommittee on Gas Phase Kinetic Data Evaluation for Atmospheric Chemistry. Data sheets have been prepared for 658 thermal and photochemical reactions, containing summaries of the available experimental data with notes giving details of the experimental procedures. For each reaction, a preferred value of the rate coefficient at 298 K is given together with a temperature dependence where possible. The selection of the preferred value is discussed and estimates of the accuracies of the rate coefficients and temperature coefficients have been made for each reaction. The data sheets are intended to provide the basic physical chemical data needed as input for calculations which model atmospheric chemistry. A table summarizing the preferred rate data is provided, together with an appendix listing the available data on enthalpies of formation of the reactant and product species. We have also included for the first time in this series of evaluations a section on heterogeneous reactions of importance in atmospheric chemistry. © *1997 American Institute of Physics and American Chemical Society.* [S0047-2689(97)00204-3]

Key words: air pollution; atmospheric chemistry; chemical kinetics; data evaluation; gas phase; heterogeneous atmospheric reactions; photoabsorption cross-section, photochemistry; quantum yield; rate coefficient.

Contents

1. Preface

This paper is the fifth supplement to the original set of critically evaluated kinetic and photochemical rate parameters for atmospheric chemistry, published by the CODATA Task Group on Gas Phase Chemical Kinetics in 1980[1] and subsequently updated by the first supplement in 1982,[2] and the second supplement in 1984.[3] The original evaluation and the first two supplements were primarily intended to furnish a kinetic data base for modeling middle atmosphere chemistry (10–55 km altitude).

In 1985 the International Union of Pure and Applied Chemistry (IUPAC) set up a group to continue and enlarge upon the work initiated by CODATA. The Subcommittee on Gas Phase Kinetic Data Evaluation for Atmospheric Chemistry is chaired by J. A. Kerr and is part of the Commission on Chemical Kinetics (I.4) of the IUPAC Physical Chemistry Division.

This subcommittee produced the third supplement in 1989,[4] and the fourth supplement in 1992,[5] in which the original data base was extended and updated to include more reactions involved in tropospheric chemistry. Since it was not possible to cope with all of the very large number of chemical reactions involved in tropospheric chemistry, it was decided to limit the coverage to those organic reactions for which kinetic or photochemical data exist for species containing up to three carbon atoms. The present fifth supplement has continued this policy in considering the reactions of organic species.

Following the pattern of the fourth supplement,[5] here we provide a data sheet for each of the reactions considered. For thermal reactions for which no new data have been published since the last data sheet was presented, we have summarized that data sheet by listing the **Preferred Values** together with the *Comments on the Preferred Values*. For thermal reactions for which new data have subsequently appeared since the data sheet was last published, we have followed our previous practice of listing only the new data, together with updated Reviews and Evaluations. For photochemical reactions for which no new data have been published we have reproduced the data sheet from the last evaluation.[5] Where new data have become available for existing photochemical reactions, we have listed only the new data. As in Supplement IV, we have also prepared a large number of data sheets for "new" thermal and photochemical reactions, which were not included in our previous evaluations.

For each reaction the data sheet includes the preferred rate coefficient with a statement of the error limits, a comment giving the basis for the recommendation, and a list of the relevant references. To the extent that this information suffices, the reader can use the present publication without need to refer to the previous publications in the series. However, it should be emphasized that in preparing the updated data sheets, we have not listed all of the previous data contained in the original evaluation[1] and the four supplements.[2–5] Consequently for many reactions, to obtain the overall picture and background to the preferred rate parameters, it is essential that the present supplement be read in conjunction with its predecessors.[1–5]

The following list of reactions, for which data sheets were prepared in previous evaluations, have now been omitted, on the grounds that they are unimportant in atmospheric chemistry:

$O + O_2 \rightarrow O_3^*$
$O_3^* + M \rightarrow O_3 + M$
$O + O_3^* \rightarrow \text{products}$
$O_2(^1\Sigma_g^+)^* + O_2 \rightarrow O_2(^1\Sigma_g^+) + O_2$
$H + O_3 \rightarrow HO + O_2$

$H + O_3 \rightarrow HO^* + O_2$
$O + H_2 \rightarrow HO + H$
$HO + H_2(\nu=1) \rightarrow H_2O + H$
$HO^* + M \rightarrow HO + M$
$HO^* + O_3 \rightarrow$ products
$O + N_2O_5 \rightarrow$ products
$N + HO \rightarrow NO + H$
$N + O_2 \rightarrow NO + O$
$N + O_2(^1\Delta_g) \rightarrow NO + O$
$N + O_3 \rightarrow NO + O_2$
$N + NO \rightarrow N_2 + O$
$N + NO_2 \rightarrow N_2O + O$
$NH_2 + HO \rightarrow$ products
$NH_2 + HO_2 \rightarrow$ products
$NO + h\nu \rightarrow$ products
$O(^1D) + CN \rightarrow$ products
$CN + O_2 \rightarrow$ products
$O + H_2S \rightarrow HO + HS$
$CH_3O_2 + SO_2 \rightarrow$ products
$F + NO_2 + M \rightarrow FONO + M$
$FO + NO_2 + M \rightarrow FONO_2 + M$
$O + HCl \rightarrow HO + Cl$
$ClO + O_2(^1\Delta_g) \rightarrow$ *sym*-ClO_3
$ClO + HCHO \rightarrow$ products
$ClONO_2 + H_2O \rightarrow HOCl + HONO_2$
$ClONO_2 + HCl \rightarrow Cl_2 + HONO_2$
$O + HBr \rightarrow HO + Br$
$O + Br_2 \rightarrow BrO + Br$

These reactions are no longer included in the present Summary of Reactions and in referring to them in previous evaluations,[1–5] it should be kept in mind that the data sheets may not be up-to-date for any particular reaction.

In this evaluation we have included for the first time in our series of evaluations a consideration of heterogeneous reactions which are involved in atmospheric chemistry. In this context we have focused upon an assessment of data relating to uptake coefficients of gas phase species upon relevant surfaces. A summary table listing the heterogeneous reactions considered is also given after the summary table for the gas-phase reactions.

The cutoff point for literature searching for this supplement was May 1994. As in our previous evaluations, we also include data which were available to us in preprint form at that point.

2. Summary of Reactions and Preferred Rate Data

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$ K
	O_x Reactions						
550	$O + O_2 + M \rightarrow O_3 + M$	6.0×10^{-34} [O_2]	(k_0)	±0.05	$6.0\times10^{-34}(T/300)^{-2.8}$ [O_2]	100–300	$\Delta n=\pm0.5$
		5.6×10^{-34} [N_2]	(k_0)	±0.05	$5.6\times10^{-34}(T/300)^{-2.8}$ [N_2]	100 300	$\Delta n=\pm0.5$
550	$O + O_3 \rightarrow 2O_2$	8.0×10^{-15}		±0.08	$8.0\times10^{-12}\exp(-2060/T)$	200–400	±200
551	$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	4.0×10^{-11}		±0.05	$3.2\times10^{-11}\exp(67/T)$	200–350	±100
551	$O(^1D) + O_3 \rightarrow O_2 + 2O(^3P)$	1.2×10^{-10}		±0.1	2.4×10^{-10}	100–400	$\Delta\log k=\pm0.05$
	$\rightarrow 2O_2(^3\Sigma_g^-)$	1.2×10^{-10}		±0.1			
552	$O_2^* + O_3 \rightarrow O + 2O_2$			See data sheet			
552	$O_2(^3\Sigma_g^-, v') + M \rightarrow O_2(^3\Sigma_g^-, v') + M$			See data sheet			
553	$O_2(^1\Delta_g) + M \rightarrow O_2(^3\Sigma_g^-) + M$	1.6×10^{-18}	($M = O_2$)	±0.2	$3.0\times10^{-18}\exp(-200/T)$	100–450	±200
		$<1.4\times10^{-19}$	($M = N_2$)				
		5×10^{-18}	($M = H_2O$)	±0.3			
		$\leqslant2\times10^{-20}$	($M = CO_2$)				
553	$O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$	3.8×10^{-15}		±0.10	$5.2\times10^{-11}\exp(-2840/T)$	280–360	±500
554	$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^3\Sigma_g^-) + M$	4.0×10^{-17}	($M = O_2$)	±0.3			
	$\rightarrow O_2(^1\Delta_g) + M$	2.0×10^{-15}	($M = N_2$)	±0.10	2.0×10^{-15}	200–350	±200
		8.0×10^{-14}	($M = O(^3P)$)	±0.3			
		4.0×10^{-12}	($M = H_2O$)	±0.3			
		4.1×10^{-13}	($M = CO_2$)	±0.10	4.1×10^{-13}	245–360	±200
555	$O_2(^1\Sigma_g^+) + O_3 \rightarrow 2O_2 + O$	2.2×10^{-11}		±0.06	2.2×10^{-11}	295–360	±300
	$\rightarrow O_2(^1\Delta_g) + O_3$						
	$\rightarrow O_2(^3\Sigma_g^-) + O_3$						
556	$O_2 + h\nu \rightarrow$ products	See data sheet					
557	$O_3 + h\nu \rightarrow$ products	See data sheet					
	HO_x Reactions						
560	$H + HO_2 \rightarrow H_2 + O_2$	5.6×10^{-12}		±0.5	5.6×10^{-12}	245–300	$\Delta\log k=\pm0.5$
	$\rightarrow 2HO$	7.2×10^{-11}		±0.1	7.2×10^{-11}	245–300	$\Delta\log k=\pm0.1$
	$\rightarrow H_2O + O$	2.4×10^{-12}		±0.5	2.4×10^{-12}	245–300	$\Delta\log k=\pm0.5$
560	$H + O_2 + M \rightarrow HO_2 + M$	5.4×10^{-32} [N_2]	(k_0)	±0.2	$5.4\times10^{-32}(T/300)^{-1.8}$ [N_2]	200–600	$\Delta n=\pm0.6$
		7.5×10^{-11}	(k_∞)	±0.3	7.5×10^{-11}	200–300	$\Delta n=\pm0.6$
		$F_c=0.55$		$\Delta F_c=\pm0.15$	$F_c=\exp(-T/498)$	200–300	
561	$O + HO \rightarrow O_2 + H$	3.3×10^{-11}		±0.1	$2.3\times10^{-11}\exp(110/T)$	220–500	±100
562	$O + HO_2 \rightarrow HO + O_2$	5.8×10^{-11}		±0.08	$2.7\times10^{-11}\exp(224/T)$	200–400	±100
562	$O + H_2O_2 \rightarrow HO + HO_2$	1.7×10^{-15}		±0.3	$1.4\times10^{-12}\exp(-2000/T)$	250–390	±1000
563	$O(^1D) + H_2 \rightarrow HO + H$	1.1×10^{-10}		±0.1	1.1×10^{-10}	200–350	±100
563	$O(^1D) + H_2O \rightarrow 2HO$	2.2×10^{-10}		±0.1	2.2×10^{-10}	200–350	±100
564	$HO + H_2 \rightarrow H_2O + H$	6.7×10^{-15}		±0.1	$7.7\times10^{-12}\exp(-2100/T)$	200–450	±200
564	$HO + HO \rightarrow H_2O + O$	1.9×10^{-12}		±0.15	$7.9\times10^{-14}(T/298)^{2.6}\exp(945/T)$	200–500	±250

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
565	$HO + HO + M \rightarrow H_2O_2 + M$	6.9×10^{-31} [N_2]	(k_0)	±0.1	$6.9\times10^{-31}(T/300)^{-0.8}$ [N_2]	200–400	$\Delta n=\pm0.5$
		2.6×10^{-11}	(k_∞)	±0.2	2.6×10^{-11}	200–300	$\Delta\log k_\infty=\pm0.2$
		$F_c=0.5$					
566	$HO + HO_2 \rightarrow H_2O + O_2$	1.1×10^{-10}		±0.1	$4.8\times10^{-11}\exp(250/T)$	250–400	±200
566	$HO + H_2O_2 \rightarrow H_2O + HO_2$	1.7×10^{-12}		±0.1	$2.9\times10^{-12}\exp(-160/T)$	240–460	±100
567	$HO + O_3 \rightarrow HO_2 + O_2$	6.7×10^{-14}		±0.15	$1.9\times10^{-12}\exp(-1000/T)$	220–450	±300
567	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.6×10^{-12}		±0.15	$2.2\times10^{-13}\exp(600/T)$	230–420	±200
567	$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$	5.2×10^{-32} [N_2]		±0.15	1.9×10^{-33} [N_2] $\exp(980/T)$	230–420	±300
		4.5×10^{-32} [O_2]		±0.15			
		See data sheet for effect of H_2O					
568	$HO_2 + O_3 \rightarrow HO + 2O_2$	2.0×10^{-15}		±0.2	$1.4\times10^{-14}\exp(-600/T)$	250–350	$+500$ -100
569	$H_2O + h\nu \rightarrow$ products	See data sheet					
569	$H_2O_2 + h\nu \rightarrow$ products	See data sheet					
	NO_x Reactions						
571	$O + NO + M \rightarrow NO_2 + M$	1.0×10^{-31} [N_2]	(k_0)	±0.1	$1.0\times10^{-31}(T/300)^{-1.6}$ [N_2]	200–300	$\Delta n=\pm0.3$
		3.0×10^{-11}	(k_∞)	±0.3	$3.0\times10^{-11}(T/300)^{0.3}$	200–1500	$\Delta n=\pm0.3$
		$F_c=0.85$			$F_c=\exp(-T/1850)$	200–300	
572	$O + NO_2 \rightarrow O_2 + NO$	9.7×10^{-12}		±0.06	$6.5\times10^{-12}\exp(120/T)$	230–350	±120
572	$O + NO_2 + M \rightarrow NO_3 + M$	9.0×10^{-32} [N_2]	(k_0)	±0.10	$9.0\times10^{-32}(T/300)^{-2.0}$ [N_2]	200–400	$\Delta n=\pm1$
		2.2×10^{-11}	(k_∞)	±0.2	2.2×10^{-11}	200–400	$\Delta n=\pm0.5$
		$F_c=0.8$			$F_c=\exp(-T/1300)$	200–400	
573	$O + NO_3 \rightarrow O_2 + NO_2$	1.7×10^{-11}		±0.3			
573	$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	2.6×10^{-11}		±0.1	$1.8\times10^{-11}\exp(107/T)$	200–350	±100
574	$O(^1D) + N_2O \rightarrow N_2 + O_2$	4.4×10^{-11}		±0.1	4.4×10^{-11}	200–350	±100
	$\rightarrow 2NO$	7.2×10^{-11}		±0.1	7.2×10^{-11}	200–350	±100
574	$HO + NH_3 \rightarrow H_2O + NH_2$	1.6×10^{-13}		±0.1	$3.5\times10^{-12}\exp(-925/T)$	230–450	±200
575	$HO + HONO \rightarrow H_2O + NO_2$	6.5×10^{-12}		±0.15	$2.7\times10^{-12}\exp(260/T)$	250–400	±260
576	$HO + HONO_2 \rightarrow H_2O + NO_3$	1.5×10^{-13}	(1 bar)	±0.1	See data sheet		
576	$HO + HO_2NO_2 \rightarrow$ products	5.0×10^{-12}		±0.2	$1.5\times10^{-12}\exp(360/T)$	240–340	$+300$ -600
577	$HO + NO + M \rightarrow HONO + M$	7.4×10^{-31} [N_2]	(k_0)	±0.10	$7.4\times10^{-31}(T/300)^{-2.4}$ [N_2]	200–400	$\Delta n=\pm0.5$
		4.5×10^{-11}	(k_∞)	±0.2	4.5×10^{-11}	200–400	$\Delta\log k=\pm0.2$
		$F_c=0.9$	(250 K)				
578	$HO + NO_2 + M \rightarrow HNO_3 + M$	2.6×10^{-30} [N_2]	(k_0)	±0.1	$2.6\times10^{-30}(T/300)^{-2.9}$ [N_2]	200–400	$\Delta n=\pm0.3$
		6.7×10^{-11}	(k_∞)	±0.10	$6.7\times10^{-11}(T/300)^{-0.6}$	200–400	$\Delta n=\pm0.5$
		$F_c=0.43$					
580	$HO + NO_3 \rightarrow HO_2 + NO_2$	2.0×10^{-11}		±0.3			
580	$HO_2 + NO \rightarrow HO + NO_2$	8.3×10^{-12}		±0.1	$3.7\times10^{-12}\exp(240/T)$	230–500	±100
581	$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$	1.8×10^{-31} [N_2]	(k_0)	±0.10	$1.8\times10^{-31}(T/300)^{-3.2}$ [N_2]	200–300	$\Delta n=\pm1$
		4.7×10^{-12}	(k_∞)	±0.2	4.7×10^{-12}	200–300	$\Delta n=\pm1$
		$F_c=0.6$			$F_c=0.6$		

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
582	$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$	1.3×10^{-20} [N_2]	(k_0/s^{-1})	±0.3	5×10^{-6} $(-10000/T)$ [N_2]	260–300	±500
		0.34	(k_∞/s^{-1})	±0.5	$2.6\times10^{15}\exp(-10900/T)$	260–300	±500
		F_c=0.6					
583	$HO_2 + NO_3 \rightarrow O_2 + HNO_3$ $\rightarrow HO + NO_2 + O_2$	4.0×10^{-12}		±0.2			
584	$NH_2 + O_2 \rightarrow$ products	$<6\times10^{-21}$					
584	$NH_2 + O_3 \rightarrow$ products	1.7×10^{-13}		±0.5	$4.9\times10^{-12}\exp(-1000/T)$	250–380	±500
585	$NH_2 + NO \rightarrow$ products	1.6×10^{-11}		±0.2	$1.6\times10^{-11}(T/298)^{-1.5}$	210–500	$\Delta n=\pm0.5$
586	$NH_2 + NO_2 \rightarrow$ products	2.0×10^{-11}		±0.2	$2.0\times10^{-11}(T/298)^{-2.0}$	250–500	$\Delta n=\pm0.7$
586	$2NO + O_2 \rightarrow 2NO_2$	2.0×10^{-38} (cm^6 molecule^{-2} s^{-1})		±0.1	$3.3\times10^{-39}\exp(530/T)$	273–600	±400
586	$NO + O_3 \rightarrow NO_2 + O_2$	1.8×10^{-14}		±0.08	$1.8\times10^{-12}\exp(-1370/T)$	195–304	±200
587	$NO + NO_2 + M \rightarrow N_2O_3 + M$	3.1×10^{-34} [N_2]	(k_0)	±0.3	$3.1\times10^{-34}(T/300)^{-7.7}$ [N_2]	208–300	$\Delta n=\pm1$
		7.9×10^{-12}	(k_∞)	±0.3	$7.9\times10^{-12}(T/300)^{1.4}$	208–300	$\Delta n=\pm0.5$
		F_c=0.6					
588	$N_2O_3 + M \rightarrow NO + NO_2 + M$	1.6×10^{-14}[N_2]	(k_0/s^{-1})	±0.4	$1.9\times10^{-7}(T/300)^{-8.7}$ $\times\exp(-4880/T)$ [N_2]	225–300	±200 $\Delta n=\pm1$
		3.6×10^{8}	(k_∞/s^{-1})	±0.3	$4.7\times10^{15}(T/300)^{0.4}\exp(-4880/T)$	225–300	±100 $\Delta n=\pm1$
		F_c=0.6					
589	$NO + NO_3 \rightarrow 2NO_2$	2.6×10^{-11}		±0.1	$1.8\times10^{-11}\exp(110/T)$	220–400	±100
590	$NO_2 + O_3 \rightarrow NO_3 + O_2$	3.2×10^{-17}		±0.06	$1.2\times10^{-13}\exp(-2450/T)$	230–360	±150
590	$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$	1.4×10^{-33} [N_2]	(k_0)	±0.3	$1.4\times10^{-33}(T/300)^{-3.8}$ [N_2]	300–500	$\Delta n=\pm1$
		1.0×10^{-12}	(k_∞)	±0.3	1.0×10^{-12}	250–300	$\Delta\log k=\pm0.3$
		F_c=0.40					
592	$N_2O_4 + M \rightarrow NO_2 + NO_2 + M$	6.1×10^{-15} [N_2]	(k_0/s^{-1})	±0.3	$1.3\times10^{-5}(T/300)^{-3.8}$ $\times\exp(-6400/T)$ [N_2]	300–500	±500
		4.4×10^{6}	(k_∞/s^{-1})	±0.4	$1.15\times10^{16}\exp(-6460/T)$	250–300	±500
		F_c=0.40					
593	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	2.7×10^{-30} [N_2]	(k_0)	±0.10	$2.7\times10^{-30}(T/300)^{-3.4}$ [N_2]	200–400	$\Delta n=\pm0.5$
		2.0×10^{-12}	(k_∞)	±0.2	$2.0\times10^{-12}(T/300)^{0.2}$	200–500	$\Delta n=\pm0.6$
		F_c=0.33			$F_c=[\exp(-T/250)+\exp(-1050/T)]$	200–500	
594	$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	9.5×10^{-20} [N_2]	(k_0/s^{-1})	±0.2	$1.0\times10^{-3}(T/300)^{-3.5}$ $\times\exp(-11000/T)$ [N_2]	200–400	$\Delta n=\pm0.5$
		6.9×10^{-2}	(k_∞/s^{-1})	±0.3	$9.7\times10^{14}(T/300)^{0.1}$ $\times\exp(-11080/T)$	200–300	$\Delta n=\pm0.2$
		F_c=0.33			$F_c=[\exp(-T/250)+\exp(-1050/T)]$	200–300	
595	$N_2O_5 + H_2O \rightarrow 2HNO_3$	$<2\times10^{-21}$					
595	$HONO + h\nu \rightarrow$ products	See data sheet					
596	$HONO_2 + h\nu \rightarrow$ products	See data sheet					
599	$HO_2NO_2 + h\nu \rightarrow$ products	See data sheet					
599	$NO_2 + h\nu \rightarrow$ products	See data sheet					
601	$NO_3 + h\nu \rightarrow$ products	See data sheet					
604	$N_2O + h\nu \rightarrow$ products	See data sheet					
605	$N_2O_5 + h\nu \rightarrow$ products	See data sheet					

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
	Organic Reactions						
607	O + CH_3 → products	1.4×10^{-10}		±0.1	1.4×10^{-10}	200–900	±100
607	O(^{1}D) + CH_4 → HO + CH_3 → HCHO + H_2	1.5×10^{-10}		±0.1	1.5×10^{-10}	200–300	±100
608	HO + CH_4 → H_2O + CH_3	6.2×10^{-15}		±0.08	$2.3\times10^{-12}\exp(-1765/T)$	240–300	±100
610	HO + C_2H_2 + M → C_2H_2OH + M	5.0×10^{-30} [N_2]	(k_0)	±0.1	$5\times10^{-30}(T/300)^{-1.5}$ [N_2]	200–300	$\Delta n=\pm1.5$
		9.0×10^{-13}	(k_∞)	±0.1	$9.0\times10^{-13}(T/300)^2$	200–300	$\Delta n=\pm1$
		$F_c=0.62$					
611	HO + C_2H_4 + M → C_2H_4OH + M	7×10^{-29} [N_2]	(k_0)	±0.3	$7\times10^{-29}(T/300)^{-3.1}$ [N_2]	200–300	$\Delta n=\pm2$
		9×10^{-12}	(k_∞)	±0.3	9×10^{-12}	200–300	$\Delta n=\pm0.5$
		$F_c=0.7$					
613	HO + C_2H_6 → H_2O + C_2H_5	2.5×10^{-13}		±0.10	$7.9\times10^{-12}\exp(-1030/T)$	240–300	±100
614	HO + C_3H_6 + M → C_3H_6OH + M	8×10^{-27} [N_2]	(k_0)	±1.0	$8\times10^{-27}(T/300)^{-3.5}$ [N_2]	200–300	$\Delta n=\pm1$
		3.0×10^{-11}	(k_∞)	±0.1	3.0×10^{-11}	200–300	$\Delta n=\pm1$
		$F_c=0.5$					
615	HO + C_3H_8 → H_2O + C_3H_7	1.10×10^{-12}		±0.08	$8.0\times10^{-12}\exp(-590/T)$	240–300	±150
617	HO + CO → H + CO_2	$1.3\times10^{-13}(1+0.6$ P/bar)		±0.1	$1.3\times10^{-13}(1+0.6$ P/bar) $\times(300/T)^{1.0}$	200–300	$\Delta\log k=\pm0.2$
618	HO + HCHO → H_2O + HCO	9.2×10^{-12}		±0.10	$8.6\times10^{-12}\exp(20/T)$	240–300	±150
619	HO + CH_3CHO → H_2O + CH_3CO	1.6×10^{-11}		±0.10	$5.6\times10^{-12}\exp(310/T)$	240–530	±200
620	HO + C_2H_5CHO → products	2.0×10^{-11}		±0.15			
620	HO + $(CHO)_2$ → H_2O + CHOCO	1.1×10^{-11}		±0.3			
621	HO + $HOCH_2CHO$ → H_2O + $HOCH_2CO$	8.0×10^{-12}		±0.3			
	→ H_2O + HOCHCHO	2.0×10^{-12}		±0.3			
621	HO + CH_3COCHO → H_2O + CH_3COCO	1.5×10^{-11}		±0.2			
622	HO + CH_3COCH_3 → H_2O + CH_3COCH_2	2.2×10^{-13}		±0.15	$2.8\times10^{-12}\exp(-760/T)$	240–300	±200
622	HO + CH_3OH → H_2O + CH_2OH	7.9×10^{-13}		±0.15	$3.1\times10^{-12}\exp(-360/T)$	240–300	±200
	→ H_2O + CH_3O	1.4×10^{-13}		±0.15			
623	HO + C_2H_5OH → H_2O + CH_2CH_2OH	1.6×10^{-13}		±0.15	$4.1\times10^{-12}\exp(-70/T)$	270–340	±200
	→ H_2O + CH_3CHOH	2.9×10^{-12}		±0.15			
	→ H_2O + CH_3CH_2O	1.6×10^{-13}		±0.15			
625	HO + n-C_3H_7OH → products	5.5×10^{-12}		±0.2			
625	HO + i-C_3H_7OH → products	5.1×10^{-12}		±0.12	$2.7\times10^{-12}\exp(190/T)$	270–340	±200
626	HO + CH_3OCH_3 → H_2O + CH_3OCH_2	2.9×10^{-12}		±0.2	$1.0\times10^{-11}\exp(-370/T)$	290–450	±200
627	HO + CH_3COCH_2OH → products	3.0×10^{-13}		±0.3			
627	HO + CH_3OOH → H_2O + CH_2OOH	1.9×10^{-12}		±0.2	$1.0\times10^{-12}\exp(190/T)$	220–430	±150
	→ H_2O + CH_3OO	3.6×10^{-12}		±0.2	$1.9\times10^{-12}\exp(190/T)$	220–430	±150
628	HO + HCOOH → products	4.5×10^{-13}		±0.15	4.5×10^{-13}	290–450	±250
628	HO + CH_3COOH → products	8×10^{-13}		±0.3			
629	HO + C_2H_5COOH → products	1.2×10^{-12}		±0.2	1.2×10^{-12}	290–450	±300
629	HO + CH_3ONO_2 → products	3.5×10^{-13}	(1 bar)	±0.10	$1.0\times10^{-14}\exp(1060/T)$ (1 bar)	290–400	±500

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
630	$HO + C_2H_5ONO_2 \rightarrow$ products	4.9×10^{-13}	(1 bar)	±0.15	$4.4\times10^{-14}\exp(720/T)$ (1 bar)	290–380	±500
630	$HO + n\text{-}C_3H_7ONO_2 \rightarrow$ products	7.3×10^{-13}	(1 bar)	±0.15	7.3×10^{-13} (1 bar)	290–370	±500
630	$HO + i\text{-}C_3H_7ONO_2 \rightarrow$ products	4.9×10^{-13}	(1 bar)	±0.25			
631	$HO + CH_3CO_3NO_2 \rightarrow$ products	1.1×10^{-13}		±0.2	$9.5\times10^{-13}\exp(-650/T)$	270–300	±400
631	$HO + CH_3COCH_2ONO_2 \rightarrow$ products	$<1\times10^{-12}$					
632	$HO + HCN \rightarrow$ products	3×10^{-14}	(1 bar)	±0.5	$1.2\times10^{-13}\exp(-400/T)$ (1 bar)	290–440	±300
632	$HO + CH_3CN \rightarrow$ products	2.2×10^{-14}	(1 bar)	±0.15	$8.1\times10^{-13}\exp(-1080/T)$ (1 bar)	250–390	±200
633	$HO_2 + CH_3O_2 \rightarrow O_2 + CH_3O_2H$	5.2×10^{-12}		±0.3	$3.8\times10^{-13}\exp(780/T)$	225–580	±500
633	$HO_2 + HOCH_2O_2 \rightarrow O_2 + HOCH_2O_2H$ $\rightarrow O_2 + HCO_2H + H_2O$	1.2×10^{-11}		±0.3	$5.6\times10^{-15}\exp(2300/T)$	275–335	±1500
634	$HO_2 + C_2H_5O_2 \rightarrow O_2 + C_2H_5O_2H$	7.7×10^{-12}		±0.2	$2.7\times10^{-13}\exp(1000/T)$	200–500	±300
635	$HO_2 + CH_3CO_3 \rightarrow O_2 + CH_3CO_3H$	1.0×10^{-11}		±0.3	$4.3\times10^{-13}\exp(1040/T)$	250–370	±500
	$\rightarrow O_3 + CH_3CO_2H$	3.6×10^{-12}		±0.3			
636	$HO_2 + HOCH_2CH_2O_2 \rightarrow$ products	1.0×10^{-11}		±0.3			
636	$HO_2 + CH_3OCH_2O_2 \rightarrow O_2 + CH_3OCH_2O_2H$ $\rightarrow O_2 + CH_3OCHO + H_2O$	See data sheet					
637	$HO_2 + CH_3COCH_2O_2 \rightarrow O_2 + CH_3COCH_2O_2H$	9.0×10^{-12}		±0.3			
637	$HO_2 + HCHO \rightarrow HOCH_2OO$	7.9×10^{-14}		±0.3	$9.7\times10^{-15}\exp(625/T)$	275–333	±600
638	$HOCH_2OO \rightarrow HO_2 + HCHO$	1.5×10^{2}	(k/s^{-1})	±0.3	$2.4\times10^{12}\exp(-7000/T)$	275–333	±2000
639	$NO_3 + CH_4 \rightarrow HNO_3 + CH_3$	$<1\times10^{-18}$					
639	$NO_3 + C_2H_2 \rightarrow$ products	$<1\times10^{-16}$					
640	$NO_3 + C_2H_4 \rightarrow$ products	2.1×10^{-16}		±0.2	$3.3\times10^{-12}\exp(-2880/T)$	270–340	±500
641	$NO_3 + C_2H_6 \rightarrow HNO_3 + C_2H_5$	$<1\times10^{-17}$					
641	$NO_3 + C_3H_6 \rightarrow$ products	9.5×10^{-15}		±0.2	$4.6\times10^{-13}\exp(-1155/T)$	296–423	±300
642	$NO_3 + C_3H_8 \rightarrow HNO_3 + C_3H_7$	$<7\times10^{-17}$					
642	$NO_3 + HCHO \rightarrow HNO_3 + HCO$	5.8×10^{-16}		±0.3			
643	$NO_3 + CH_3CHO \rightarrow HNO_3 + CH_3CO$	2.7×10^{-15}		±0.2	$1.4\times10^{-12}\exp(-1860/T)$	260–370	±500
643	$NO_3 + CH_3COCH_3 \rightarrow HNO_3 + CH_3COCH_2$	$<3\times10^{-17}$					
644	$NO_3 + CH_3OH \rightarrow$ products	2.4×10^{-16}		±0.5	$1.3\times10^{-12}\exp(-2560/T)$	290–480	±700
644	$NO_3 + C_2H_5OH \rightarrow$ products	$<2\times10^{-15}$					
644	$NO_3 + i\text{-}C_3H_7OH \rightarrow$ products	$<5\times10^{-15}$					
645	$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	1.0×10^{-30} [N_2]	(k_0)	±0.2	$1.0\times10^{-30}(T/300)^{-3.3}$ [N_2]	200–300	$\Delta n=\pm1$
		1.8×10^{-12}	(k_∞)	±0.3	$1.8\times10^{-12}(T/300)^{1.1}$	200–300	$\Delta n=\pm1$
		$F_c=0.27$					
646	$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	3.8×10^{-15}	(1 bar air)	±0.5			
		1.9×10^{-14}	(0.133 bar air)	±0.5			
646	$C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$	5.9×10^{-29} [N_2]	(k_0)	±0.3	$5.9\times10^{-29}(T/300)^{-3.8}$ [N_2]	200–300	$\Delta n=\pm1$
		7.8×10^{-12}	(k_∞)	±0.2	7.8×10^{-12}	200–300	$\Delta\log k=\pm0.2$
		$F_c=0.54$			$F_c=\{0.58\exp(-T/1250)$ $+0.42\exp(-T/183)\}$	200–300	
647	$n\text{-}C_3H_7 + O_2 + M \rightarrow n\text{-}C_3H_7O_2 + M$	8×10^{-12}	(k_∞)	±0.2	8×10^{-12}	200–300	$\Delta\log k=\pm0.2$
647	$i\text{-}C_3H_7 + O_2 + M \rightarrow i\text{-}C_3H_7O_2 + M$	1.1×10^{-11}	(k_∞)	±0.3	1.1×10^{-11}	200–300	$\Delta\log k=\pm0.3$

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
648	$CH_3COCH_2 + O_2 + M \rightarrow CH_3COCH_2O_2 + M$	1.5×10^{-12}	(k_∞)	±0.5			
648	$HCO + O_2 \rightarrow CO + HO_2$	5.5×10^{-12}		±0.15	5.5×10^{-12}	200–400	±150
648	$CH_3CO + O_2 + M \rightarrow CH_3CO_3 + M$	5.0×10^{-12}	(k_∞)	±0.5	5.0×10^{-12}	200–300	$\Delta\log k=\pm0.5$
649	$CH_2OH + O_2 \rightarrow HCHO + HO_2$	9.4×10^{-12}		±0.12			
649	$CH_3CHOH + O_2 \rightarrow CH_3CHO + HO_2$	1.9×10^{-11}		±0.3			
650	$CH_2CH_2OH + O_2 \rightarrow$ products	3.0×10^{-12}		±0.3			
650	$CH_3O + O_2 \rightarrow HCHO + HO_2$	1.9×10^{-15}		±0.2	$7.2\times10^{-14}\exp(-1080/T)$	298–610	±300
651	$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	9.5×10^{-15}		±0.2	$6.0\times10^{-14}\exp(-550/T)$	295–425	±300
651	$n\text{-}C_3H_7O + O_2 \rightarrow C_2H_5CHO + HO_2$	8×10^{-15}		±0.5			
652	$i\text{-}C_3H_7O + O_2 \rightarrow CH_3COCH_3 + HO_2$	8×10^{-15}		±0.3	$1.5\times10^{-14}\exp(-200/T)$	290–390	±200
652	$CH_3OCH_2O + O_2 \rightarrow CH_3OCHO + HO_2$	See data sheet					
652	$CH_3OCH_2O + M \rightarrow CH_3OCHO + H + M$						
652	$CH_3COCH_2O + O_2 \rightarrow CH_3COCHO + HO_2$	See data sheet					
652	$CH_3COCH_2O + M \rightarrow CH_3CO + HCHO + M$						
653	$CH_3 + O_3 \rightarrow$ products	2.5×10^{-12}		±0.3	$5.1\times10^{-12}\exp(-210/T)$	240–400	±200
653	$CH_3O + NO + M \rightarrow CH_3ONO + M$	1.6×10^{-29} [N_2]	(k_0)	±0.1	$1.6\times10^{-29}(T/300)^{-3.5}$ [N_2]	200–400	$\Delta n=\pm0.5$
		3.6×10^{-11}	(k_∞)	±0.5	$3.6\times10^{-11}(T/300)^{-0.6}$	200–400	$\Delta n=\pm0.5$
		$F_c=0.6$					
653	$CH_3O + NO \rightarrow HCHO + HNO$	4×10^{-12}			$4\times10^{-12}(T/300)^{-0.7}$	200–400	$\Delta n=\pm0.5$
654	$C_2H_5O + NO + M \rightarrow C_2H_5ONO + M$	4.4×10^{-11}	(k_∞)	±0.3	4.4×10^{-11}	200–300	$\Delta n=\pm0.5$
654	$C_2H_5O + NO \rightarrow CH_3CHO + HNO$	1.3×10^{-11}					
655	$i\text{-}C_3H_7O + NO + M \rightarrow i\text{-}C_3H_7ONO + M$	3.4×10^{-11}	(k_∞)	±0.3	3.4×10^{-11}	200–300	$\Delta n=\pm0.5$
655	$i\text{-}C_3H_7O + NO \rightarrow (CH_3)_2CO + HNO$	6.5×10^{-12}		±0.5			
655	$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M$	2.8×10^{-29} [N_2]	(k_0)	±0.3	$2.8\times10^{-29}(T/300)^{-4.5}$ [N_2]	200–400	$\Delta n=\pm1$
		2.0×10^{-11}	(k_∞)	±0.3	2.0×10^{-11}	200–400	$\Delta n=\pm0.5$
		$F_c=0.44$					
655	$CH_3O + NO_2 \rightarrow HCHO + HONO$	See data sheet					
656	$C_2H_5O + NO_2 + M \rightarrow C_2H_5ONO_2 + M$	2.8×10^{-11}	(k_∞)	±0.3	2.8×10^{-11}	200–300	$\Delta n=\pm0.5$
656	$C_2H_5O + NO_2 \rightarrow CH_3CHO + HONO$	See data sheet					
656	$i\text{-}C_3H_7O + NO_2 + M \rightarrow i\text{-}C_3H_7ONO_2 + M$	3.5×10^{-11}	(k_∞)	±0.3	3.5×10^{-11}	200–300	$\Delta n=\pm0.5$
656	$i\text{-}C_3H_7O + NO_2 \rightarrow (CH_3)_2CO + HONO$	See data sheet					
657	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	7.6×10^{-12}		±0.1	$4.2\times10^{-12}\exp(180/T)$	240–360	±180
658	$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$	8.7×10^{-12}		±0.2			
658	$C_2H_5O_2 + NO\ (+M) \rightarrow C_2H_5ONO_2\ (+M)$	$\leq1.2\times10^{-13}$	(1 bar)				
658	$HOCH_2CH_2O_2 + NO \rightarrow HOCH_2CH_2O + NO_2$	9×10^{-12}		±0.5			
659	$n\text{-}C_3H_7O_2 + NO \rightarrow n\text{-}C_3H_7O + NO_2$	4.9×10^{-12}		±0.3			
659	$n\text{-}C_3H_7O_2 + NO(+M) \rightarrow n\text{-}C_3H_7ONO_2\ (+M)$	1.0×10^{-13}	(1 bar)	±0.5			
659	$i\text{-}C_3H_7O_2 + NO \rightarrow i\text{-}C_3H_7O + NO_2$	4.8×10^{-12}		±0.3			
659	$i\text{-}C_3H_7O_2 + NO\ (+M) \rightarrow i\text{-}C_3H_7ONO_2\ (+M)$	2.1×10^{-13}	(1 bar)	±0.5			
660	$CH_3CO_3 + NO \rightarrow CH_3 + CO_2 + NO_2$	2.0×10^{-11}		±0.2	2.0×10^{-11}	280–325	±600
661	$C_2H_5CO_3 + NO \rightarrow C_2H_5 + CO_2 + NO_2$	2.0×10^{-11}		±0.5			

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
661	$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$	2.5×10^{-30} [N_2]	(k_0)	±0.3	$2.5\times10^{-30}(T/300)^{-5.5}$ [N_2]	250–350	$\Delta n=\pm1$
		7.5×10^{-12}	(k_∞)	±0.3	7.5×10^{-12}	250–350	$\Delta n=\pm0.5$
		$F_c=0.36$					
662	$CH_3O_2NO_2 + M \rightarrow CH_3O_2 + NO_2 + M$	6.8×10^{-19} [N_2]	(k_0/s^{-1})	±0.3	$9\times10^{-5}\exp(-9690/T)$ [N_2]	250–300	±500
		4.5	(k_∞/s^{-1})	±0.3	$1.1\times10^{16}\exp(-10560/T)$	250–300	±500
		$F_c=0.36$					
663	$C_2H_5O_2 + NO_2 + M \rightarrow C_2H_5O_2NO_2 + M$	1.3×10^{-29} [N_2]	(k_0)	±0.3	$1.3\times10^{-29}(T/300)^{-6.2}$ [N_2]	200–300	$\Delta n=\pm1$
		8.8×10^{-12}	(k_∞)	±0.3	8.8×10^{-12}	200–300	$\Delta\log k=\pm0.3$
		$F_c=0.31$			$F_c=0.31$	250–300	
664	$C_2H_5O_2NO_2 + M \rightarrow C_2H_5O_2 + NO_2 + M$	1.4×10^{-17} [N_2]	(k_0/s^{-1})	±0.5	$4.8\times10^{-4}\exp(-9285/T)$ [N_2]	250–300	±1000
		5.4	(k_∞/s^{-1})	±0.5	$8.8\times10^{15}\exp(-10440/T)$	250–300	±1000
		$F_c=0.31$			$F_c=0.31$	250–300	
664	$CH_3CO_3 + NO_2 + M \rightarrow CH_3CO_3NO_2 + M$	2.7×10^{-28} [N_2]	(k_0)	±0.4	$2.7\times10^{-28}(T/300)^{-7.1}$ [N_2]	250–300	$\Delta n=\pm2$
		1.2×10^{-11}	(k_∞)	±0.2	$1.2\times10^{-11}(T/300)^{-0.9}$	250–300	$\Delta n=\pm1$
		$F_c=0.3$					
665	$CH_3CO_3NO_2 + M \rightarrow CH_3CO_3 + NO_2 + M$	1.1×10^{-20} [N_2]	(k_0/s^{-1})	±0.4	$4.9\times10^{-3}\exp(-12100/T)$ [N_2]	300–330	±1000
		3.8×10^{-4}	(k_∞/s^{-1})	±0.3	$5.4\times10^{16}\exp(-13830/T)$	300–330	±300
		$F_c=0.3$					
666	$C_2H_5CO_3NO_2 + M \rightarrow C_2H_5CO_3 + NO_2 + M$	4.4×10^{-4}	(k_∞/s^{-1})	±0.4	$2\times10^{15}\exp(-12800/T)$	300–315	±500
667	$CH_3O_2 + NO_3 \rightarrow$ products	No recommendation (see data sheet)					
	$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2$						
	$\rightarrow 2CH_3O + O_2$	3.7×10^{-13}		±0.12	$1.1\times10^{-13}\exp(365/T)$	200–400	±200
	$\rightarrow CH_3OOCH_3 + O_2$						
669	$CH_3O_2 + CH_3CO_3 \rightarrow CH_3O + CH_3CO_2 + O_2$	1.1×10^{-11}		±0.3	$5.1\times10^{-12}\exp(272/T)$	250–370	±300
	$\rightarrow CH_3CO_2H + HCHO + O_2$	1.8×10^{-12}		±0.5			
670	$CH_3O_2 + CH_3COCH_2O_2$						
	$\rightarrow CH_3OH + CH_3COCHO + O_2$						
	$\rightarrow HCHO + CH_3COCH_2OH + O_2$	3.8×10^{-12}		±0.3			
	$\rightarrow CH_3O + CH_3COCH_2O + O_2$						
670	$HOCH_2O_2 + HOCH_2O_2$						
	$\rightarrow HCOOH + CH_2(OH)_2 + O_2$	7.0×10^{-13}		±0.3	$5.7\times10^{-14}\exp(750/T)$	275–325	±750
	$\rightarrow 2HOCH_2O + O_2$	5.5×10^{-12}		±0.3			
671	$C_2H_5O_2 + C_2H_5O_2 \rightarrow C_2H_5OH + CH_3CHO + O_2$						
	$\rightarrow 2C_2H_5O + O_2$	6.4×10^{-14}		±0.12	6.4×10^{-14}	250–450	+300
	$\rightarrow C_2H_5OOC_2H_5 + O_2$						−100
672	$CH_3OCH_2O_2 + CH_3OCH_2O_2$						
	$\rightarrow CH_3OCH_2OH + CH_3OCHO + O_2$	7×10^{-13}		±0.3			
	$\rightarrow 2CH_3OCH_2O + O_2$	1.4×10^{-12}		±0.3			
673	$CH_3CO_3 + CH_3CO_3 \rightarrow 2CH_3CO_2 + O_2$	1.6×10^{-11}		±0.5	$2.8\times10^{-12}\exp(530/T)$	250–370	±500
674	$CH_3CO_3 + CH_3COCH_2O_2$						
	$\rightarrow CH_3COOH + CH_3COCHO + O_2$	5.0×10^{-12}		±0.3			
	$\rightarrow CH_3 + CO_2 + CH_3COCH_2O + O_2$						

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
674	$HOCH_2CH_2O_2 + HOCH_2CH_2O_2$					
	$\rightarrow HOCH_2CH_2OH + HOCH_2CHO + O_2$	1.15×10^{-12}	±0.3			
	$\rightarrow 2HOCH_2CH_2O + O_2$	1.15×10^{-12}	±0.3			
675	$n\text{-}C_3H_7O_2 + n\text{-}C_3H_7O_2$					
	$\rightarrow n\text{-}C_3H_7OH + C_2H_5CHO + O_2$ $\rightarrow 2n\text{-}C_3H_7O + O_2$	3×10^{-13}	±0.5			
675	$i\text{-}C_3H_7O_2 + i\text{-}C_3H_7O_2$					
	$\rightarrow i\text{-}C_3H_7OH + (CH_3)_2CO + O_2$	4.4×10^{-16}	±0.3	$1.6\times10^{-12}\exp(-2200/T)$	300–400	±300
	$\rightarrow 2i\text{-}C_3H_7O + O_2$	5.6×10^{-16}	±0.3			
676	$CH_3COCH_2O_2 + CH_3COCH_2O_2$					
	$\rightarrow CH_3COCH_2OH + CH_3COCHO + O_2$	2.0×10^{-12}	0.5			
	$\rightarrow 2CH_3COCH_2O + O_2$	6.0×10^{-12}	0.3			
678	$RCHOO + H_2O \rightarrow RCOOH + H_2O$	No recommendations (see data sheet)				
678	$RCHOO + NO_2 \rightarrow RCHO + NO_3$					
678	$RCHOO + SO_2 \rightarrow$ products					
678	$RCHOO + HCHO \rightarrow$ products					
680	$O_3 + C_2H_2 \rightarrow$ products	1×10^{-20}	±1.0			
681	$O_3 + C_2H_4 \rightarrow$ products	1.6×10^{-18}	±0.10	$9.1\times10^{-15}\exp(-2580/T)$	180–360	±100
682	$O_3 + C_3H_6 \rightarrow$ products	1.0×10^{-17}	±0.10	$5.5\times10^{-15}\exp(-1880/T)$	230–370	±200
684	$HCHO + h\nu \rightarrow$ products	See data sheet				
685	$CH_3CHO + h\nu \rightarrow$ products	See data sheet				
686	$C_2H_5CHO + h\nu \rightarrow$ products	See data sheet				
687	$(CHO)_2 + h\nu \rightarrow$ products	See data sheet				
688	$CH_3COCHO + h\nu \rightarrow$ products	See data sheet				
690	$CH_3COCH_3 + h\nu \rightarrow$ products	See data sheet				
691	$CH_3OOH + h\nu \rightarrow$ products	See data sheet				
692	$CH_3ONO_2 + h\nu \rightarrow$ products	See data sheet				
693	$C_2H_5ONO_2 + h\nu \rightarrow$ products	See data sheet				
694	$n\text{-}C_3H_7ONO_2 + h\nu \rightarrow$ products	See data sheet				
694	$i\text{-}C_3H_7ONO_2 + h\nu \rightarrow$ products	See data sheet				
695	$CH_3O_2NO_2 + h\nu \rightarrow$ products	See data sheet				
696	$CH_3CO_3NO_2 + h\nu \rightarrow$ products	See data sheet				
	SO_x Reactions					
698	$O + CS \rightarrow CO + S$	2.1×10^{-11}	±0.1	$2.7\times10^{-10}\exp(-760/T)$	150–300	±250
698	$O + CH_3SCH_3 \rightarrow CH_3SO + CH_3$	5.0×10^{-11}	±0.1	$1.3\times10^{-11}\exp(409/T)$	270–560	±100
699	$O + CS_2 \rightarrow$ products	3.6×10^{-12}	±0.2	$3.2\times10^{-11}\exp(-650/T)$	200–500	±100
700	$O + CH_3SSCH_3 \rightarrow CH_3SO + CH_3S$	1.3×10^{-10}	±0.3	$5.5\times10^{-11}\exp(250/T)$	290–570	±100
700	$O + OCS \rightarrow SO + CO$	1.2×10^{-14}	±0.2	$1.6\times10^{-11}\exp(-2150/T)$	220–500	±150
701	$O + SO_2 + M \rightarrow SO_3 + M$	1.4×10^{-33} [N_2] (k_0)	±0.3	$4.0\times10^{-32}\exp(-1000/T)$ [N_2]	200–400	±200
701	$S + O_2 \rightarrow SO + O$	2.1×10^{-12}	±0.2	2.1×10^{-12}	230–400	±200
701	$S + O_3 \rightarrow SO + O_2$	1.2×10^{-11}	±0.3			
702	$Cl + H_2S \rightarrow HCl + HS$	5.7×10^{-11}	±0.3	5.7×10^{-11}	210–350	±100
702	$HO + H_2S \rightarrow H_2O + HS$	4.8×10^{-12}	±0.08	$6.3\times10^{-12}\exp(-80/T)$	200–300	±80

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
703	$HO + SO_2 + M \rightarrow HOSO_2 + M$	4.0×10^{-31} [N_2]	(k_0)	±0.3	$4.0\times10^{-31}(T/300)^{-3.3}$ [N_2]	300–400	$\Delta n=\pm1$
		2×10^{-12}	(k_∞)	±0.3	2×10^{-12}	200–300	$\Delta\log k=\pm0.3$
		$F_c=0.45$					
703	$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$	4.3×10^{-13}		±0.1	$1.3\times10^{-12}\exp(-330/T)$	290–420	±200
704	$HO + OCS \rightarrow$ products	2.0×10^{-15}		±0.3	$1.1\times10^{-13}\exp(-1200/T)$	250–500	±500
704	$HO + CS_2 + M \rightarrow HOCS_2 + M$	8×10^{-31} [N_2]	(k_0)	±0.5	8×10^{-31} [N_2]	270–300	$\Delta\log k=\pm0.5$
		8×10^{-12}	(k_∞)	±0.5	8×10^{-12}	250–300	$\Delta\log k=\pm0.5$
		$F_c=0.8$					
704	$HO + CS_2 \rightarrow HS + OCS$	$<2\times10^{-15}$					
705	$HOCS_2 + M \rightarrow HO + CS_2 + M$	4.8×10^{-14} [N_2]	(k_0/s^{-1})	±0.5	$1.6\times10^{-6}\exp(-5160/T)$ [N_2]	250–300	±500
		4.8×10^{5}	(k_∞/s^{-1})	±0.5	$1.6\times10^{13}\exp(-5160/T)$	250–300	±500
		$F_c=0.8$					
706	$HOCS_2 + O_2 \rightarrow$ products	3.0×10^{-14}		±0.3	3.0×10^{-14}	240–350	$\Delta\log k=\pm0.3$
707	$HO + CH_3SH \rightarrow$ products	3.3×10^{-11}		±0.10	$9.9\times10^{-12}\exp(356/T)$	240–430	±100
708	$HO + CH_3SCH_3 \rightarrow H_2O + CH_2SCH_3$	4.8×10^{-12}		±0.10	$1.13\times10^{-11}\exp(-254/T)$	250–400	±150
	$\rightarrow CH_3S(OH)CH_3$	1.7×10^{-12}	(1 bar air)		See data sheet		
709	$HO + CH_3SSCH_3 \rightarrow$ products	2.3×10^{-10}		±0.10	$7.0\times10^{-11}\exp(350/T)$	250–370	±200
710	$HO_2 + SO_2 \rightarrow$ products	$\leqslant1\times10^{-18}$					
710	$NO_3 + H_2S \rightarrow$ products	$<1\times10^{-15}$					
711	$NO_3 + CS_2 \rightarrow$ products	$<1\times10^{-15}$					
711	$NO_3 + OCS \rightarrow$ products	$<1\times10^{-16}$					
711	$NO_3 + SO_2 \rightarrow$ products	$<1\times10^{-19}$					
712	$NO_3 + CH_3SH \rightarrow$ products	9.2×10^{-13}		±0.15	9.2×10^{-13}	250–370	±400
712	$NO_3 + CH_3SCH_3 \rightarrow$ products	1.1×10^{-12}		±0.15	$1.9\times10^{-13}\exp(520/T)$	250–380	±200
713	$NO_3 + CH_3SSCH_3 \rightarrow$ products	7×10^{-13}		±0.3	7×10^{-13}	300–380	±500
713	$HS + O_2 \rightarrow$ products	$\leqslant4\times10^{-19}$					
714	$HS + O_3 \rightarrow HSO + O_2$	3.7×10^{-12}		±0.2	$9.5\times10^{-12}\exp(-280/T)$	290–450	±250
714	$HS + NO + M \rightarrow HSNO + M$	2.4×10^{-31} [N_2]	(k_0)	±0.3	$2.4\times10^{-31}(T/300)^{-2.5}$ [N_2]	200–300	$\Delta n=\pm1$
		2.7×10^{-11}	(k_∞)	±0.5	2.7×10^{-11}	200–300	$\Delta\log k=\pm0.5$
		$F_c=0.6$					
715	$HS + NO_2 \rightarrow HSO + NO$	5.8×10^{-11}		±0.3	$2.6\times10^{-11}\exp(240/T)$	220–450	±200
715	$HSO + O_2 \rightarrow$ products	$\leqslant2.0\times10^{-17}$					
716	$HSO + O_3 \rightarrow$ products	1.1×10^{-13}		±0.3			
716	$HSO + NO \rightarrow$ products	$\leqslant1.0\times10^{-15}$					
717	$HSO + NO_2 \rightarrow$ products	9.6×10^{-12}		±0.3			
717	$HSO_2 + O_2 \rightarrow$ products	3.0×10^{-13}		±0.8			
717	$SO + O_2 \rightarrow SO_2 + O$	7.6×10^{-17}		±0.15	$1.6\times10^{-13}\exp(-2280/T)$	230–420	±500
718	$SO + O_3 \rightarrow SO_2 + O_2$	8.9×10^{-14}		±0.10	$4.5\times10^{-12}\exp(-1170/T)$	230–420	±150
718	$SO + NO_2 \rightarrow SO_2 + NO$	1.4×10^{-11}		±0.1	1.4×10^{-11}	210–360	±100
719	$SO_3 + H_2O \rightarrow$ products	$<6\times10^{-15}$					
719	$SO_3 + NH_3 \rightarrow$ products	6.9×10^{-11}		±0.3			
720	$CS + O_2 \rightarrow$ products	2.9×10^{-19}		±0.6			
720	$CS + O_3 \rightarrow OCS + O_2$	3.0×10^{-16}		±0.5			
720	$CS + NO_2 \rightarrow OCS + NO$	7.6×10^{-17}		±0.5			
721	$CH_2SH + O_2 \rightarrow$ products	6.6×10^{-12}		±0.3			

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta \log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
721	$CH_2SH + O_3 \rightarrow$ products	3.5×10^{-11}		±0.3			
722	$CH_2SH + NO \rightarrow$ products	1.5×10^{-11}		±0.3			
722	$CH_2SH + NO_2 \rightarrow$ products	4.4×10^{-11}		±0.5			
723	$CH_3S + O_2 + M \rightarrow CH_3SOO + M$	See data sheet					
724	$CH_3SOO + M \rightarrow CH_3S + O_2 + M$	See data sheet					
724	$CH_3S + O_3 \rightarrow$ products	5.4×10^{-12}		±0.2	$2.0\times10^{-12}\exp(290/T)$	290–360	±200
725	$CH_3S + NO + M \rightarrow CH_3SNO + M$	$3.2\times10^{-29}\,[N_2]$	(k_0)	±0.3	$3.2\times10^{-29}\,(T/300)^{-4}\,[N_2]$	250–450	$\Delta n=\pm2$
		4×10^{-11}	(k_∞)	±0.5	4×10^{-11}	250–450	$\Delta \log k=\pm0.5$
		$F_c=0.60$			$F_c=\exp(-T/580)$		
726	$CH_3S + NO_2 \rightarrow CH_3SO + NO$	5.8×10^{-11}		±0.15	$2.2\times10^{-11}\exp(320/T)$	240–350	±300
727	$CH_3SO + O_3 \rightarrow$ products	6.0×10^{-13}		±0.3			
727	$CH_3SO + NO_2 \rightarrow$ products	1.2×10^{-11}		±0.5			
728	$CH_3SOO + O_3 \rightarrow$ products	$< 8\times10^{-13}$ (228 K)					
728	$CH_3SOO + NO \rightarrow$ products				1.1×10^{-11}	227–255	$\Delta \log k=\pm0.3$
729	$CH_3SOO + NO_2 \rightarrow$ products				2.2×10^{-11}	227–246	$\Delta \log k=\pm0.3$
729	$CH_3SCH_2 + O_2 \rightarrow CH_3SCH_2O_2$	5.7×10^{-12}	(1 bar)	±0.4			
730	$CH_3SCH_2O_2 + NO \rightarrow CH_3SCH_2O + NO_2$	1.9×10^{-11}		±0.4			
730	$CH_3SCH_2O_2 + CH_3SCH_2O_2 \rightarrow$ products	$\leqslant8\times10^{-12}$					
731	$CH_3SS + O_3 \rightarrow$ products	4.6×10^{-12}		±0.3			
731	$CH_3SS + NO_2 \rightarrow$ products	1.8×10^{-11}		±0.3			
732	$CH_3SSO + NO_2 \rightarrow$ products	4.5×10^{-12}		±0.3			
732	$O_3 + CH_3SCH_3 \rightarrow$ products	$<1\times10^{-18}$					
733	$OCS + h\nu \rightarrow$ products	See data sheet					
734	$CS_2 + h\nu \rightarrow$ products	See data sheet					
735	$CH_3SSCH_3 + h\nu \rightarrow$ products	See data sheet					
735	$CH_3SNO + h\nu \rightarrow$ products	See data sheet					
	FO_x Reactions						
737	$O + FO \rightarrow O_2 + F$	2.7×10^{-11}		±0.3			
737	$O + FO_2 \rightarrow O_2 + FO$	5×10^{-11}		±0.7			
737	$\left.\begin{array}{l} O(^1D) + HF \rightarrow HO + F \\ \quad\rightarrow O(^3P) + HF \end{array}\right\}$	1×10^{-10}		±0.5			
738	$O(^1D) + COF_2 \rightarrow CO_2 + F_2$	2.2×10^{-11}		±0.2			
	$\rightarrow O(^3P) + COF_2$	5.2×10^{-11}		±0.2			
739	$O(^1D) + CH_3F \rightarrow$ products	1.6×10^{-10}		±0.2			
739	$O(^1D) + CH_2F_2 \rightarrow$ products	5.1×10^{-11}		±0.3			
739	$O(^1D) + CHF_3 \rightarrow$ products	9.8×10^{-12}		±0.3			
739	$O(^1D) + CH_3CH_2F \rightarrow$ products	2.6×10^{-10}		±0.3			
739	$O(^1D) + CH_3CHF_2 \rightarrow$ products	2.0×10^{-10}		±0.3			
739	$O(^1D) + CH_3CF_3 \rightarrow$ products	1.0×10^{-10}		±0.3			
739	$O(^1D) + CH_2FCF_3 \rightarrow$ products	4.9×10^{-11}		±0.3			
739	$O(^1D) + CHF_2CF_3 \rightarrow$ products	1.2×10^{-10}		±0.3			
740	$F + H_2 \rightarrow HF + H$	2.6×10^{-11}		±0.1	$1.4\times10^{-10}\exp(-500/T)$	200–375	±200
740	$F + H_2O \rightarrow HF + HO$	1.4×10^{-11}		±0.1	1.4×10^{-11}	240–370	±200

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/ K
741	$F + O_2 + M \rightarrow FO_2 + M$	5.8×10^{-33} [N_2]	(k_0)	±0.3	$5.8\times10^{-33}(T/300)^{-1.7}$ [N_2]	100–400	$\Delta n=\pm0.5$
		1.2×10^{-10}	(k_∞)	±0.3	1.2×10^{-10}	100–400	$\Delta\log k_\infty=\pm0.3$
		$F_c\simeq0.5$			$F_c\simeq0.5$	100–400	
742	$FO_2 + M \rightarrow F + O_2 + M$	1.5×10^{-17} [N_2]	(k_0/s^{-1})	±0.3	8.4×10^{-9} $(T/300)^{-1.25}$ $\times\exp(-5990/T)$ [N_2]	315–420	±500 $\Delta n=\pm0.5$
		3.1×10^{5}	(k_∞/s^{-1})	±0.3	1.7×10^{14} $(T/300)^{0.45}$ $\times\exp(-5990/T)$	315–420	±500 $\Delta n=\pm0.5$
		$F_c\simeq0.5$			$F_c\approx0.5$	315–420	
743	$F + O_3 \rightarrow FO + O_2$	1.0×10^{-11}		±0.25	$2.2\times10^{-11}\exp(-230/T)$	250–365	±200
744	$F + HONO_2 \rightarrow HF + NO_3$	2.3×10^{-11}		±0.1	$6.0\times10^{-12}\exp(400/T)$	260–320	±200
744	$F + CH_4 \rightarrow HF + CH_3$	8.0×10^{-11}		±0.2	$3.0\times10^{-10}\exp(-400/T)$	250–450	±200
745	$HO + CH_3F \rightarrow H_2O + CH_2F$	2.0×10^{-14}		±0.15	$1.6\times10^{-12}\exp(-1305/T)$	240–300	±400
746	$HO + CH_2F_2 \rightarrow H_2O + CHF_2$	1.1×10^{-14}		±0.10	$2.0\times10^{-12}\exp(-1545/T)$	240–300	±200
747	$HO + CHF_3 \rightarrow H_2O + CF_3$	2.7×10^{-16}		±0.2	$6.0\times10^{-13}\exp(-2295/T)$	240–300	±300
748	$HO + CF_4 \rightarrow HOF + CF_3$	$<2\times10^{-18}$					
749	$HO + CH_3CH_2F \rightarrow$ products	2.0×10^{-13}		±0.2	$2.4\times10^{-12}\exp(-740/T)$	240–300	±300
750	$HO + CH_3CHF_2 \rightarrow$ products	3.6×10^{-14}		$^{+0.10}_{-0.20}$	$1.0\times10^{-12}\exp(-990/T)$	240–300	$^{+200}_{-400}$
751	$HO + CH_3CF_3 \rightarrow H_2O + CH_2CF_3$	1.3×10^{-15}		±0.15	$1.05\times10^{-12}\exp(-1990/T)$	240–300	±300
752	$HO + CH_2FCH_2F \rightarrow H_2O + CH_2FCHF$	1.1×10^{-13}		±0.3			
753	$HO + CH_2FCHF_2 \rightarrow$ products	1.5×10^{-14}		±0.2	$3.3\times10^{-12}\exp(-1610/T)$	270–340	±300
754	$HO + CH_2FCF_3 \rightarrow H_2O + CHFCF_3$	4.2×10^{-15}		±0.2	$7.3\times10^{-13}\exp(-1540/T)$	240–300	±300
755	$HO + CHF_2CHF_2 \rightarrow H_2O + CF_2CHF_2$	5.9×10^{-15}		±0.3	$1.4\times10^{-12}\exp(-1630/T)$	270–340	±300
756	$HO + CHF_2CF_3 \rightarrow H_2O + CF_2CF_3$	1.9×10^{-15}		±0.2	$4.9\times10^{-13}\exp(-1655/T)$	240–300	±300
757	$HO + CHF_2CF_2CH_2F \rightarrow$ products	7.2×10^{-15}		±0.3	$2.1\times10^{-12}\exp(-1690/T)$	270–340	±300
758	$HO + CF_3CF_2CH_2F \rightarrow H_2O + CF_3CF_2CHF$	6×10^{-15}		±0.3			
759	$HO + CF_3CHFCHF_2 \rightarrow$ products	4.8×10^{-15}		±0.3	$1.1\times10^{-12}\exp(-1620/T)$	270–340	±300
760	$HO + CF_3CH_2CF_3 \rightarrow H_2O + CF_3CHCF_3$	3.5×10^{-16}		±0.3	$7.9\times10^{-13}\exp(-2305/T)$	270–340	±400
761	$HO + CF_3CHFCF_3 \rightarrow H_2O + CF_3CFCF_3$	1.6×10^{-15}		±0.2	$4.5\times10^{-13}\exp(-1675/T)$	270–463	±300
762	$HO + CHF_2OCHF_2 \rightarrow H_2O + CHF_2OCF_2$	2.9×10^{-15}		±0.3			
762	$HO + HCOF \rightarrow H_2O + FCO$	$<1\times10^{-14}$					
763	$HO + CHF_2CHO \rightarrow$ products	1.6×10^{-12}		±0.2			
763	$HO + CF_3CHO \rightarrow H_2O + CF_3CO$	6.0×10^{-13}		±0.2			
764	$HO + CF_3COOH \rightarrow$ products	1.4×10^{-13}		±0.20	1.4×10^{-13}	283–348	$\Delta\log k=\pm0.20$
765	$HO_2 + CH_2FO_2 \rightarrow O_2 + CH_2FO_2H$ $\rightarrow O_2 + HCOF + H_2O$	See data sheet					
765	$HO_2 + CF_3CHFO_2$ $\rightarrow O_2 + CF_3CHFO_2H$ $\rightarrow O_2 + CF_3COF + H_2O$	3.8×10^{-12}		±0.3	$1.8\times10^{-13}\exp(910/T)$	210–365	±300
766	$FO + O_3 \rightarrow$ products	No recommendation (see data sheet)					
767	$FO + NO \rightarrow F + NO_2$	2.2×10^{-11}		±0.15	$8.2\times10^{-12}\exp(300/T)$	300–850	±200
767	$FO + FO \rightarrow$ products	1.0×10^{-11}		±0.2	1.0×10^{-11}	298–435	±250
768	$FO_2 + O_3 \rightarrow$ products	$<3.4\times10^{-16}$					
768	$FO_2 + NO \rightarrow FNO + O_2$	1.5×10^{-12}		±0.5			
769	$FO_2 + NO_2 \rightarrow$ products	1.0×10^{-13}		±0.5			
769	$FO_2 + CO \rightarrow$ products	$<5.1\times10^{-16}$					
770	$FO_2 + CH_4 \rightarrow$ products	$<4.1\times10^{-15}$					

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
770	$CF_3 + O_2 + M \rightarrow CF_3O_2 + M$	1.9×10^{-29} [N_2]	(k_0)	±0.2	$1.9\times10^{-29}(T/300)^{-4.7}$ [N_2]	200–300	$\Delta n=\pm1$
		1.0×10^{-11}	(k_∞)	±0.3	1.0×10^{-11}	200–400	$\Delta\log k_\infty=\pm0.3$
		$F_c=0.6$					
*	$CF_3O \rightarrow COF_2 + F$	$<10^{-5}$	(k/s^{-1})				
771	$CF_3O + O_2 \rightarrow COF_2 + FO_2$	$<1\times10^{-18}$			$<1\times10^{-10}\exp(-5600/T)$	250–370	
772	$CF_3O + O_3 \rightarrow CF_3O_2 + O_2$	2.5×10^{-14}		±1	$2\times10^{-12}\exp(-1300/T)$	250–370	±600
773	$CF_3O + H_2O \rightarrow CF_3OH + HO$	$<2\times10^{-17}$			$<3\times10^{-12}\exp(-3600/T)$	250–380	
773	$CF_3O + NO \rightarrow COF_2 + FNO$	5.4×10^{-11}		±0.1	$3.7\times10^{-11}\exp(110/T)$	230–390	±100
774	$CF_3O + CH_4 \rightarrow CF_3OH + CH_3$	2.1×10^{-14}		±0.1	$2.5\times10^{-12}\exp(-1420/T)$	230–380	±200
775	$CF_3O + C_2H_6 \rightarrow CF_3OH + C_2H_5$	1.2×10^{-12}		±0.1	$4.7\times10^{-12}\exp(-400/T)$	230–360	±200
777	$CH_2FO + O_2 \rightarrow HCOF + HO_2$	See data sheet					
777	$CH_2FO + M \rightarrow HCOF + H + M$						
777	$CH_3CF_2O + O_2 \rightarrow$ products	See data sheet					
777	$CH_3CF_2O + M \rightarrow CH_3 + COF_2 + M$						
777	$CH_2FCHFO + O_2 \rightarrow CH_2FCOF + HO_2$	See data sheet					
777	$CH_2FCHFO + M \rightarrow CH_2F + HCOF + M$						
777	$CF_3CHFO + O_2 \rightarrow CF_3COF + HO_2$	See data sheet					
777	$CF_3CHFO + M \rightarrow CF_3 + HCOF + M$						
777	$CF_3CF_2O + O_2 \rightarrow$ products	See data sheet					
777	$CF_3CF_2O + M \rightarrow CF_3 + COF_2 + M$						
781	$CH_2FO_2 + NO \rightarrow CH_2FO + NO_2$	1.3×10^{-11}		±0.3			
781	$CHF_2O_2 + NO \rightarrow CHF_2O + NO_2$	1.3×10^{-11}		±0.3			
781	$CF_3O_2 + NO \rightarrow CF_3O + NO_2$	1.6×10^{-11}		±0.15	$1.6\times10^{-11}(T/298)^{-1.2}$	230–430	$\Delta\log k=\pm0.15$
781	$CH_2FCHFO_2 + NO \rightarrow CH_2FCHFO + NO_2$	$>9\times10^{-12}$					
781	$CHF_2CF_2O_2 + NO \rightarrow CHF_2CF_2O + NO_2$	$>1\times10^{-11}$					
781	$CF_3CHFO_2 + NO \rightarrow CF_3CHFO + NO_2$	1.3×10^{-11}		±0.3			
781	$CF_3CF_2O_2 + NO \rightarrow CF_3CF_2O + NO_2$	$>1\times10^{-11}$					
784	$CF_3O_2 + O_3 \rightarrow CF_3O + 2O_2$	$<3\times10^{-15}$					
785	$CF_3O_2 + NO_2 + M \rightarrow CF_3O_2NO_2 + M$	4.5×10^{-29} [N_2]	(k_0)	±0.3	$4.5\times10^{-29}(T/300)^{-6.4}$ [N_2]	220–300	$\Delta\log n=\pm1$
		7.5×10^{-12}	(k_∞)	±0.5	7.5×10^{-12}	200–300	$\Delta\log k_\infty=\pm0.5$
		$F_c=0.28$			$F_c=0.28$	220–300	
786	$CF_3O_2NO_2 + M \rightarrow CF_3O_2 + NO_2 + M$	3.6×10^{-19} [N_2]	(k_0/s^{-1})	±0.4	$5\times10^{-1}(T/300)^{-6}$ $\times\exp(-12460/T)$ [N_2]	233–373	±500
		5.6×10^{-2}	(k_∞/s^{-1})	±0.5	$1.2\times10^{17}\exp(-12580/T)$	233–373	±500
		$F_c=0.28$			$F_c=0.28$	220–300	
786	$CH_2FO_2+CH_2FO_2 \rightarrow CH_2FOH + HCOF + O_2$ $\rightarrow 2CH_2FO + O_2$	$(2.0\text{–}4.0)\times10^{-12}$			$(2.0\text{–}4.0)\times10^{-13}\exp(700/T)$	220–380	
787	$CHF_2O_2 + CHF_2O_2 \rightarrow CHF_2OH + COF_2 + O_2$ $\rightarrow 2CHF_2O + O_2$	$(2.5\text{–}5)\times10^{-12}$					
788	$CF_3O_2 + CF_3O_2 \rightarrow 2CF_3O + O_2$	1.7×10^{-12}		±0.2			
789	$CF_3O_2 + CF_3CHFO_2 \rightarrow CF_3OOCHFCF_3 + O_2$ $\rightarrow CF_3O + CF_3CHFO + O_2$	8×10^{-12}		±0.5			
790	$CHF_2CF_2O_2 + CHF_2CF_2O_2$ $\rightarrow CHF_2CF_2OOCF_2CHF_2 + O_2$ $\rightarrow 2CHF_2CF_2O + O_2$	$\leqslant3\times10^{-12}$					

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
791	$CF_3CHFO_2 + CF_3CHFO_2$ $\rightarrow CF_3CHFOH + CF_3COF + O_2$ $\rightarrow 2CF_3CHFO + O_2$	5.9×10^{-12}		±0.3	$7.8\times10^{-13}\exp(605/T)$	210–375	±200
792	$CF_3CF_2O_2 + CF_3CF_2O_2 \rightarrow 2CF_3CF_2O + O_2$	$\leq2\times10^{-12}$					
792	$HCOF + h\nu \rightarrow$ products	See data sheet					
794	$COF_2 + h\nu \rightarrow$ products	See data sheet					
794	$CF_3CHO + h\nu \rightarrow$ products	See data sheet					
795	$CF_3COF + h\nu \rightarrow$ products	See data sheet					
	ClO_x Reactions						
797	$O + HOCl \rightarrow HO + ClO$	1.3×10^{-13}		±0.7	$1.0\times10^{-11}\exp(-1300/T)$	200–300	±1000
797	$O + ClO \rightarrow Cl + O_2$	3.8×10^{-11}		±0.1	3.8×10^{-11}	200–300	±250
798	$O + OClO \rightarrow O_2 + ClO$	1.0×10^{-13}		±0.3	$2.4\times10^{-12}\exp(-960/T)$	240–400	±300
798	$O + OClO + M \rightarrow ClO_3 + M$	1.8×10^{-31} [N_2]	(k_0)	±0.3	$1.8\times10^{-31}(T/298)^{-1}$ [N_2]	250–300	$\Delta n=\pm0.5$
		3.1×10^{-11}	(k_∞)	±0.3	$3.1\times10^{-11}(T/298)^{1}$	250–300	$\Delta n=\pm1$
		$F_c=0.48$					
799	$O + Cl_2O \rightarrow ClO + ClO$	4.5×10^{-12}		±0.15	$2.7\times10^{-11}\exp(-530/T)$	230–380	±200
800	$O + ClONO_2 \rightarrow$ products	2.0×10^{-13}		±0.1	$3.0\times10^{-12}\exp(-800/T)$	213–295	±200
800	$O(^1D) + CHF_2Cl \rightarrow$ products	1.0×10^{-10}		±0.15	1.0×10^{-10}	175–340	$\Delta\log k=\pm0.15$
800	$O(^1D) + CHFCl_2 \rightarrow$ products	1.9×10^{-10}		±0.2	1.9×10^{-10}	175–340	$\Delta\log k=\pm0.2$
800	$O(^1D) + CH_3CF_2Cl \rightarrow$ products	2.2×10^{-10}		±0.2			
800	$O(^1D) + CH_3CFCl_2 \rightarrow$ products	2.6×10^{-10}		±0.2			
800	$O(^1D) + CH_2ClCF_3 \rightarrow$ products	1.2×10^{-10}		±0.2			
800	$O(^1D) + CH_2ClCF_2Cl \rightarrow$ products	1.6×10^{-10}		±0.3			
800	$O(^1D) + CHFClCF_3 \rightarrow$ products	8.6×10^{-11}		±0.2			
800	$O(^1D) + CHCl_2CF_3 \rightarrow$ products	2.0×10^{-10}		±0.2			
801	$O(^1D) + CF_2Cl_2 \rightarrow$ products	1.4×10^{-10}		±0.1			
802	$O(^1D) + CFCl_3 \rightarrow$ products	2.3×10^{-10}		±0.1			
803	$O(^1D) + CCl_4 \rightarrow$ products	3.3×10^{-10}		±0.1			
803	$O(^1D) + COFCl \rightarrow$ products	1.9×10^{-10}		±0.3			
803	$O(^1D) + COCl_2 \rightarrow$ products	3.6×10^{-10}		±0.3			
804	$Cl + H_2 \rightarrow HCl + H$	1.6×10^{-14}		±0.1	$3.7\times10^{-11}\exp(-2300/T)$	200–300	±200
805	$Cl + HO_2 \rightarrow HCl + O_2$	3.2×10^{-11}		±0.2	$1.8\times10^{-11}\exp(170/T)$	250–420	±250
	$\rightarrow ClO + HO$	9.1×10^{-12}		±0.3	$4.1\times10^{-11}\exp(-450/T)$	250–420	±250
805	$Cl + H_2O_2 \rightarrow HCl + HO_2$	4.1×10^{-13}		±0.2	$1.1\times10^{-11}\exp(-980/T)$	265–424	±500
806	$Cl + O_2 + M \rightarrow ClOO + M$	1.4×10^{-33} [N_2]	(k_0)	±0.2	$1.4\times10^{-33}(T/300)^{-3.9}$ [N_2]	160–300	$\Delta n=\pm1$
		1.6×10^{-33} [O_2]	(k_0)	±0.2	$1.6\times10^{-33}(T/300)^{-2.9}$ [O_2]	160–300	$\Delta n=\pm1$
806	$ClOO + M \rightarrow Cl + O_2 + M$	6.2×10^{-13} [N_2]	(k_0/s^{-1})	±0.3	$2.8\times10^{-10}\exp(-1820/T)$ [N_2]	200–300	±200
807	$Cl + CO + M \rightarrow ClCO + M$	1.3×10^{-33} [N_2]	(k_0)	±0.3	$1.3\times10^{-33}(T/300)^{-3.8}$ [N_2]	185–300	$\Delta n=\pm1$
808	$ClCO + M \rightarrow Cl + CO + M$	2.0×10^{-14} [N_2]	(k_0/s^{-1})	±0.4	$4.1\times10^{-10}\exp(-2960/T)$ [N_2]	185–300	±200
808	$Cl + O_3 \rightarrow ClO + O_2$	1.2×10^{-11}		±0.06	$2.9\times10^{-11}\exp(-260/T)$	205–298	±100
809	$Cl + HONO_2 \rightarrow HCl + NO_3$	$<2.0\times10^{-16}$					
809	$Cl + NO_3 \rightarrow ClO + NO_2$	2.4×10^{-11}		±0.2	2.4×10^{-11}	200–300	±400
810	$Cl + OClO \rightarrow ClO + ClO$	5.8×10^{-11}		±0.1	$3.4\times10^{-11}\exp(160/T)$	298–450	±200

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta\langle E/R \rangle$ K
810	$Cl + Cl_2O \rightarrow Cl_2 + ClO$	9.6×10^{-11}		±0.1	$6.2\times10^{-11}\exp(130/T)$	233–373	±130
811	$Cl + Cl_2O_2 \rightarrow Cl_2 + ClOO$	1.0×10^{-10}		±0.3	1.0×10^{-10}	230–298	±300
811	$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$	1.2×10^{-11}		±0.12	$6.8\times10^{-12}\exp(160/T)$	219–298	±200
812	$Cl + CH_4 \rightarrow HCl + CH_3$	1.0×10^{-13}		±0.08	$9.6\times10^{-12}\exp(-1350/T)$	200–300	±250
813	$Cl + C_2H_2 + M \rightarrow C_2H_2Cl + M$	5.7×10^{-30} [N_2]	(k_0)	±0.3	$5.7\times10^{-30}(T/300)^{-3}$ [N_2]	200–300	$\Delta n=\pm1$
		2.3×10^{-10}	(k_∞)	±0.3	2.3×10^{-10}	200–400	$\Delta n=\pm1$
		$F_c=0.6$					
814	$Cl + C_2H_4 + M \rightarrow C_2H_4Cl + M$	1.6×10^{-29} [air]	(k_0)	±0.5	$1.6\times10^{-29}(T/300)^{-3.5}$ [air]	250–300	$\Delta n=\pm1$
		3×10^{-10}	(k_∞)	±0.3	3×10^{-10}	250–300	$\Delta n=\pm1$
		$F_c=0.6$					
814	$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	5.9×10^{-11}		±0.06	$8.1\times10^{-11}\exp(-95/T)$	220–600	±100
815	$Cl + C_3H_8 \rightarrow HCl + C_3H_7$	1.4×10^{-10}		±0.12	$1.2\times10^{-10}\exp(40/T)$	220–600	±200
816	$Cl + HCHO \rightarrow HCl + HCO$	7.3×10^{-11}		±0.06	$8.2\times10^{-11}\exp(-34/T)$	200–500	±100
816	$Cl + CH_3CHO \rightarrow HCl + CH_3CO$	7.2×10^{-11}		±0.15	7.2×10^{-11}	210–340	±300
817	$Cl + C_2H_5CHO \rightarrow$ products	1.2×10^{-10}		±0.3			
817	$Cl + CH_3COCH_3 \rightarrow HCl + CH_3COCH_2$	3.5×10^{-12}		±0.3			
817	$Cl + CH_3OH \rightarrow HCl + CH_2OH$	5.5×10^{-11}		±0.15	5.5×10^{-11}	200–573	±200
818	$Cl + C_2H_5OH \rightarrow$ products	9.4×10^{-11}		±0.2			
818	$Cl + n\text{-}C_3H_7OH \rightarrow$ products	1.5×10^{-10}		±0.2			
819	$Cl + i\text{-}C_3H_7OH \rightarrow$ products	8.4×10^{-11}		±0.3			
819	$Cl + CH_3OOH \rightarrow$ products	5.9×10^{-11}		±0.5			
820	$Cl + HCOOH \rightarrow$ products	2.0×10^{-13}		±0.2			
820	$Cl + CH_3COOH \rightarrow$ products	2.8×10^{-14}		±0.3			
820	$Cl + CH_3ONO_2 \rightarrow$ products	2.4×10^{-13}		±0.3			
821	$Cl + C_2H_5ONO_2 \rightarrow$ products	4.7×10^{-12}		±0.2			
821	$Cl + n\text{-}C_3H_7ONO_2 \rightarrow$ products	2.7×10^{-11}		±0.2			
821	$Cl + i\text{-}C_3H_7ONO_2 \rightarrow$ products	5.8×10^{-12}		±0.3			
821	$Cl + CH_3C(O)OONO_2 \rightarrow$ products	$<2\times10^{-14}$					
822	$Cl + CH_3CN \rightarrow$ products	$\leqslant2\times10^{-15}$					
822	$Cl + HC(O)Cl \rightarrow HCl + ClCO$	7.8×10^{-13}		±0.15	$1.2\times10^{-11}\exp(-815/T)$	265–325	±300
823	$Cl + CH_3F \rightarrow HCl + CH_2F$	3.5×10^{-13}		±0.15	$1.7\times10^{-11}\exp(-1160/T)$	273–368	±500
823	$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$	4.9×10^{-13}		±0.15	$3.3\times10^{-11}\exp(-1250/T)$	233–322	±300
824	$Cl + CH_2F_2 \rightarrow HCl + CHF_2$	7.3×10^{-14}		±0.5	$1.5\times10^{-11}\exp(-1580/T)$	281–368	±500
825	$Cl + CH_2FCl \rightarrow HCl + CHFCl$	1.1×10^{-13}		±0.3	$1.0\times10^{-11}\exp(-1340/T)$	273–368	±500
825	$Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$	3.6×10^{-13}		±0.15	$2.8\times10^{-11}\exp(-1300/T)$	270–370	±300
826	$Cl + CHF_2Cl \rightarrow HCl + CF_2Cl$	1.9×10^{-15}		±0.15			
827	$Cl + CHFCl_2 \rightarrow HCl + CFCl_2$	2.1×10^{-14}		±0.3			
827	$Cl + CHCl_3 \rightarrow HCl + CCl_3$	7.6×10^{-14}		±0.3	$4.9\times10^{-12}\exp(-1240/T)$	240–330	±400
828	$Cl + CH_3CH_2F \rightarrow HCl + CH_3CHF$	6.7×10^{-12}		±0.5	$1.5\times10^{-11}\exp(-240/T)$	281–368	±500
	$\rightarrow HCl + CH_2CH_2F$	7.3×10^{-13}		±0.5	$1.2\times10^{-11}\exp(-830/T)$	281–368	±500
828	$Cl + CH_3CHF_2 \rightarrow HCl + CH_3CF_2$	2.7×10^{-13}		±0.15	$6.8\times10^{-12}\exp(-960/T)$	280–360	±500
	$\rightarrow HCl + CH_2CHF_2$	2.5×10^{-15}		±0.5	$7.6\times10^{-12}\exp(-2395/T)$	280–360	±500
829	$Cl + CH_2FCH_2F \rightarrow HCl + CHFCH_2F$	7.7×10^{-13}		±0.5	$2.7\times10^{-11}\exp(-1060/T)$	280–360	±500
830	$Cl + CH_3CF_3 \rightarrow HCl + CH_2CF_3$	2.6×10^{-17}		±0.5	$1.0\times10^{-11}\exp(-3830/T)$	281–368	±500
830	$Cl + CH_2FCHF_2 \rightarrow HCl + CH_2FCF_2$	2.5×10^{-14}		±0.5	$4.8\times10^{-12}\exp(-1560/T)$	281–368	±500
	$\rightarrow HCl + CHFCHF_2$	2.5×10^{-14}		±0.5	$6.7\times10^{-12}\exp(-1670/T)$	281–368	±500

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta \log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
831	$Cl + CH_3CF_2Cl \rightarrow HCl + CH_2CF_2Cl$	4.0×10^{-16}		±0.15			
832	$Cl + CH_3CFCl_2 \rightarrow HCl + CH_2CFCl_2$	2.3×10^{-15}		±0.1	$1.0\times10^{-12}\exp(-1800/T)$	298–376	±500
832	$Cl + CH_3CCl_3 \rightarrow HCl + CH_2CCl_3$	$<4\times10^{-14}$					
833	$Cl + CH_2FCF_3 \rightarrow HCl + CHFCF_3$	1.5×10^{-15}		±0.1			
833	$Cl + CHF_2CHF_2 \rightarrow HCl + CF_2CHF_2$	2.2×10^{-15}		±0.2	$7.9\times10^{-12}\exp(-2440/T)$	280–360	±500
834	$Cl + CHF_2CF_3 \rightarrow HCl + CF_2CF_3$	2.4×10^{-16}		±0.2			
835	$Cl + CHFClCF_3 \rightarrow HCl + CFClCF_3$	2.7×10^{-15}		±0.1	$1.1\times10^{-12}\exp(-1800/T)$	276–376	±500
835	$Cl + CHCl_2CF_3 \rightarrow HCl + CCl_2CF_3$	1.2×10^{-14}		±0.1	$4.4\times10^{-12}\exp(-1750/T)$	276–382	±500
836	$Cl + OCS \rightarrow SCl + CO$	$<1.0\times10^{-16}$					
837	$Cl + CS_2 + O_2 \rightarrow$ products	$\leq4\times10^{-15}$	(1 bar air)				
838	$Cl + CH_3SCH_3 \rightarrow$ products	3.3×10^{-10}	(1 bar N_2)	±0.2			
839	$HO + Cl_2 \rightarrow HOCl + Cl$	6.7×10^{-14}		±0.1	$1.4\times10^{-12}\exp(-900/T)$	250–330	±400
839	$HO + HCl \rightarrow H_2O + Cl$	8.1×10^{-13}		±0.1	$2.4\times10^{-12}\exp(-330/T)$	200–300	±150
840	$HO + HOCl \rightarrow ClO + H_2O$	5.0×10^{-13}		±0.5	$3.0\times10^{-12}\exp(-500/T)$	200–300	±500
840	$HO + ClO \rightarrow HO_2 + Cl$ $\rightarrow HCl + O_2$	1.7×10^{-11}		±0.2	$1.1\times10^{-11}\exp(120/T)$	200–373	±150
841	$HO + OClO \rightarrow HOCl + O_2$	7.0×10^{-12}		±0.3	$4.5\times10^{-13}\exp(800/T)$	290–480	±200
841	$HO + ClNO_2 \rightarrow HOCl + NO_2$	3.6×10^{-14}		±0.3	$2.4\times10^{-12}\exp(-1250/T)$	260–350	±300
842	$HO + ClONO_2 \rightarrow$ products	3.9×10^{-13}		±0.2	$1.2\times10^{-12}\exp(-330/T)$	246–387	±200
843	$HO + CH_3Cl \rightarrow H_2O + CH_2Cl$	4.2×10^{-14}		±0.10	$3.8\times10^{-12}\exp(-1340/T)$	240–300	±200
844	$HO + CH_2FCl \rightarrow H_2O + CHFCl$	4.4×10^{-14}		±0.10	$2.0\times10^{-12}\exp(-1135/T)$	240–300	±200
844	$HO + CH_2Cl_2 \rightarrow H_2O + CHCl_2$	1.2×10^{-13}		±0.20	$2.7\times10^{-12}\exp(-920/T)$	240–300	±300
846	$HO + CHF_2Cl \rightarrow H_2O + CF_2Cl$	4.6×10^{-15}		±0.10	$7.8\times10^{-13}\exp(-1530/T)$	240–300	±200
847	$HO + CHFCl_2 \rightarrow H_2O + CFCl_2$	3.0×10^{-14}		±0.10	$8.8\times10^{-13}\exp(-1010/T)$	240–300	±200
847	$HO + CHCl_3 \rightarrow H_2O + CCl_3$	1.0×10^{-13}		±0.10	$9.3\times10^{-13}\exp(-660/T)$	240–300	±100
848	$HO + CF_2Cl_2 \rightarrow HOCl + CF_2Cl$	$<7\times10^{-18}$			$<1\times10^{-12}\exp(-3540/T)$	250–478	
848	$HO + CFCl_3 \rightarrow HOCl + CFCl_2$	$<5\times10^{-18}$			$<1\times10^{-12}\exp(-3650/T)$	250–480	
849	$HO + CCl_4 \rightarrow HOCl + CCl_3$	$<5\times10^{-16}$			$<1\times10^{-12}\exp(-2260/T)$	250–300	
849	$HO + C_2HCl_3 \rightarrow$ products	2.2×10^{-12}		±0.10	$5.0\times10^{-13}\exp(445/T)$	230–420	±200
849	$HO + C_2Cl_4 \rightarrow$ products	1.7×10^{-13}		±0.10	$9.4\times10^{-12}\exp(-1200/T)$	300–420	±200
850	$HO + CH_3CF_2Cl \rightarrow H_2O + CH_2CF_2Cl$	3.0×10^{-15}		±0.10	$9.2\times10^{-13}\exp(-1705/T)$	240–300	±200
851	$HO + CH_3CFCl_2 \rightarrow H_2O + CH_2CFCl_2$	5.9×10^{-15}		±0.15	$7.0\times10^{-13}\exp(-1425/T)$	240–300	±200
852	$HO + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$	9.5×10^{-15}		±0.10	$1.2\times10^{-12}\exp(-1440/T)$	240–300	±200
853	$HO + CH_2ClCF_3 \rightarrow H_2O + CHClCF_3$	1.3×10^{-14}		±0.2	$5.2\times10^{-13}\exp(-1100/T)$	260–380	±250
853	$HO + CH_2ClCF_2Cl \rightarrow H_2O + CHClCF_2Cl$	1.6×10^{-14}		±0.3	$3.2\times10^{-12}\exp(-1580/T)$	250–350	±500
854	$HO + CHFClCF_3 \rightarrow H_2O + CFClCF_3$	9.5×10^{-15}		±0.20	$5.4\times10^{-13}\exp(-1205/T)$	240–300	±300
855	$HO + CHCl_2CF_3 \rightarrow H_2O + CCl_2CF_3$	3.6×10^{-14}		±0.15	$5.5\times10^{-13}\exp(-815/T)$	240–300	±200
856	$HO + CHFClCF_2Cl \rightarrow H_2O + CFClCF_2Cl$	1.2×10^{-14}		±0.3	$8.4\times10^{-13}\exp(-1255/T)$	298–460	±400
856	$HO + CHCl_2CF_2Cl \rightarrow H_2O + CCl_2CF_2Cl$	5.1×10^{-14}		±0.3	$1.2\times10^{-12}\exp(-940/T)$	298–460	±400
857	$HO + CHFClCFCl_2 \rightarrow H_2O + CFClCFCl_2$	1.7×10^{-13}		±0.3	$4.1\times10^{-12}\exp(-945/T)$	270–340	±400
857	$HO + CHCl_2CF_2CF_3 \rightarrow H_2O + CCl_2CF_2CF_3$	2.5×10^{-14}		±0.15	$1.1\times10^{-12}\exp(-1130/T)$	270–400	±300
858	$HO + CHFClCF_2CF_2Cl \rightarrow H_2O + CFClCF_2CF_2Cl$	8.9×10^{-15}		±0.10	$5.5\times10^{-13}\exp(-1230/T)$	290–400	±300
858	$HO + CH_3CF_2CFCl_2 \rightarrow H_2O + CH_2CF_2CFCl_2$	2.4×10^{-15}		±0.3	$7.0\times10^{-13}\exp(-1690/T)$	290–370	±300
858	$HO + HC(O)Cl \rightarrow H_2O + ClCO$	$<5\times10^{-13}$					
858	$HO + COCl_2 \rightarrow$ products	$<5\times10^{-15}$					

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)/$ K
859	$HO + CH_2ClCHO \rightarrow$ products	3.1×10^{-12}		±0.20			
860	$HO + CHFClCHO \rightarrow$ products	2.1×10^{-12}		±0.20			
860	$HO + CHCl_2CHO \rightarrow$ products	2.4×10^{-12}		±0.20			
861	$HO + CF_2ClCHO \rightarrow H_2O + CF_2ClCO$	8.2×10^{-13}		±0.25			
861	$HO + CFCl_2CHO \rightarrow H_2O + CFCl_2CO$	1.2×10^{-12}		±0.20			
862	$HO + CCl_3CHO \rightarrow H_2O + CCl_3CO$	1.1×10^{-12}		±0.15			
863	$HO + CH_3COCl \rightarrow H_2O + CH_2COCl$	9×10^{-15}		±1.0			
863	$HO + CHF_2OCHClCF_3 \rightarrow$ products	2.1×10^{-14}		±0.5			
864	$HO + CHF_2OCF_2CHFCl \rightarrow$ products	1.6×10^{-14}		±0.5	$6.1\times10^{-13}\exp(-1080/T)$	300–430	±500
865	$HO_2 + CF_3CCl_2O_2 \rightarrow O_2 + CF_3CCl_2O_2H$	1.9×10^{-12}		±0.3			
865	$HO_2 + CH_2ClO_2 \rightarrow O_2 + CH_2ClO_2H$	5.0×10^{-12}		±0.3	$3.2\times10^{-13}\exp(820/T)$	250–600	±300
866	$NO_3 + HCl \rightarrow HNO_3 + Cl$	$<5\times10^{-17}$					
866	$NO_3 + C_2HCl_3 \rightarrow$ products	2.9×10^{-16}		±0.3			
866	$NO_3 + C_2Cl_4 \rightarrow$ products	$<1\times10^{-16}$					
868	$ClO + HO_2 \rightarrow HOCl + O_2$ $\rightarrow HCl + O_3$	5.0×10^{-12}		±0.15	$4.6\times10^{-13}\exp(710/T)$	200–300	±300
868	$ClO + O_3 \rightarrow ClOO + O_2$	$<1.5\times10^{-17}$					
	$\rightarrow OClO + O_2$	$<1\times10^{-18}$					
868	$ClO + NO \rightarrow Cl + NO_2$	1.7×10^{-11}		±0.1	$6.2\times10^{-12}\exp(294/T)$	202–415	±100
869	$ClO + NO_2 + M \rightarrow ClONO_2 + M$	1.6×10^{-31} [N_2]	(k_0)	±0.1	$1.6\times10^{-31}(T/300)^{-3.4}$ [N_2]	200–300	$\Delta n=\pm1$
		2×10^{-11}	(k_∞)	±0.3	2×10^{-11}	200–300	$\Delta\log k=\pm0.3$
		$F_c=0.5$			$F_c=\exp(-T/430)$	200–300	
870	$ClO + NO_3 \rightarrow ClOO + NO_2$ $\rightarrow OClO + NO_2$	4.7×10^{-13}		±0.2	4.7×10^{-13}	210–350	±400
871	$ClO + ClO \rightarrow Cl_2 + O_2$	4.8×10^{-15}		±0.2	$1.0\times10^{-12}\exp(-1590/T)$	260–390	±500
	$\rightarrow Cl + ClOO$	8.0×10^{-15}		±0.2	$3.0\times10^{-11}\exp(-2450/T)$	260–390	±500
	$\rightarrow Cl + OClO$	3.5×10^{-15}		±0.2	$3.5\times10^{-13}\exp(-1370/T)$	260–390	±500
872	$ClO + ClO + M \rightarrow Cl_2O_2 + M$	1.7×10^{-32} [N_2]	(k_0)	±0.1	$1.7\times10^{-32}(T/300)^{-4}$ [N_2]	200–300	$\Delta n=\pm1.5$
		5.4×10^{-12}	(k_∞)	±0.3	5.4×10^{-12}	200–300	$\Delta\log k=\pm0.3$
		$F_c=0.6$					
874	$Cl_2O_2 + M \rightarrow ClO + ClO + M$	2.2×10^{-18} [N_2]	(k_0/s^{-1})	±0.3	$1\times10^{-6}\exp(-8000/T)$[$N_2$]	260–310	±900
		6.7×10^{2}	(k_∞/s^{-1})	±0.3	$4.8\times10^{15}\exp(-8820/T)$	260–310	$\pm$ 500875
875	$ClO + OClO + M \rightarrow Cl_2O_3 + M$	6.2×10^{-32} [N_2]	(k_0)	±0.3	$6.2\times10^{-32}(T/300)^{-4.7}$ [N_2]	200–300	$\Delta n=\pm1$
		2.4×10^{-11}	(k_∞)	±0.3	2.4×10^{-11}	200–300	$\Delta\log k_\infty=\pm0.3$
		$F_c=0.6$			$F_c=0.6$	200–300	
876	$Cl_2O_3 + M \rightarrow ClO + OClO + M$	2.8×10^{-18} [N_2]	(k_0/s^{-1}; 226 K)	$\pm$ 0.5 (226 K)			
876	$ClO + CH_3O_2 \rightarrow ClOO + CH_3O$	1.6×10^{-12}		±0.3	$4.9\times10^{-12}\exp(-330/T)$	225–355	±200
	$\rightarrow CH_3OCl + O_2$	6.3×10^{-13}		±0.3	$2.6\times10^{-13}\exp(260/T)$	225–355	±250
	$\rightarrow OClO + CH_3O$	$<1\times10^{-15}$	(200 K)				
877	$ClO + CH_3SCH_3 \rightarrow$ products	9×10^{-15}		±0.5			
877	$OClO + O_3 \rightarrow ClO_3 + O_2$	3.0×10^{-19}		±0.4	$2.1\times10^{-12}\exp(-4700/T)$	262–298	±1000
878	$OClO + NO \rightarrow NO_2 + ClO$	3.4×10^{-13}		±0.3			
878	$OClO + NO_3 + M \rightarrow O_2ClONO_2 + M$	1×10^{-31} [He]	(k_0; 220 K)		±0.4		
879	$Cl_2O_2 + O_3 \rightarrow ClO + ClOO + O_2$	$<1\times10^{-19}$	(200 K)				

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
879	$CF_2Cl + O_2 + M \rightarrow CF_2ClO_2 + M$	1.4×10^{-29} [N_2]	(k_0)	±0.5	$1.4\times10^{-29}(T/300)^{-5}$ [N_2]	200–300	$\Delta n=\pm2$
		9×10^{-12}	(k_∞)	±0.5	9×10^{-12}	200–300	$\Delta\log k=\pm0.5$
		F_c=0.6					
880	$CFCl_2 + O_2 + M \rightarrow CFCl_2O_2 + M$	5.5×10^{-30} [N_2]	(k_0)	±0.3	$5.5\times10^{-30}(T/300)^{-6}$ [N_2]	200–300	$\Delta n=\pm2$
		9×10^{-12}	(k_∞)	±0.5	9×10^{-12}	200–300	$\Delta n=\pm1$
		F_c=0.6					
881	$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$	9×10^{-31} [N_2]	(k_0)	±0.3	$9\times10^{-31}(T/300)^{-6}$ [N_2]	200–300	$\Delta n=\pm1$
		3×10^{-12}	(k_∞)	±0.4	3×10^{-12}	200–300	$\Delta\log k=\pm0.4$
		F_c=0.6					
777	$CHFClO + O_2 \rightarrow COFCl + HO_2$	See data sheet					
777	$CHFClO + M \rightarrow HCOF + Cl + M$						
777	$CF_2ClO + O_2 \rightarrow$ products	See data sheet					
*	$CF_2ClO + M \rightarrow COF_2 + Cl + M$	7×10^5	(k/s^{-1})	±1.0	$3\times10^{13}\exp(-5250/T)$	220–300	±1000
777	$CFCl_2O + O_2 \rightarrow$ products	See data sheet					
*	$CFCl_2O + M \rightarrow COFCl + Cl + M$	7×10^5	(k/s^{-1})	±1.0	$3\times10^{13}\exp(-5250/T)$	220–300	±1000
*	$CCl_3O \rightarrow COCl_2 + Cl$	8×10^6	(k/s^{-1})	±1.0	$4\times10^{13}\exp(-4600/T)$	220–300	±1000
777	$CF_2ClCH_2O + O_2 \rightarrow CF_2ClCHO + HO_2$	See data sheet					
777	$CF_2ClCH_2O + M \rightarrow CF_2Cl + HCHO + M$						
777	$CFCl_2CH_2O + O_2 \rightarrow CFCl_2CHO + HO_2$	See data sheet					
777	$CFCl_2CH_2O + M \rightarrow CFCl_2 + HCHO + M$						
777	$CF_3CFClO + O_2 \rightarrow$ products	See data sheet					
777	$CF_3CFClO + M \rightarrow CF_3COF + Cl + M$						
777	$CF_3CCl_2O + O_2 \rightarrow$ products	See data sheet					
777	$CF_3CCl_2O + M \rightarrow CF_3COCl + Cl + M$						
777	$CF_3CF_2CCl_2O + O_2 \rightarrow$ products	See data sheet					
777	$CF_3CF_2CCl_2O + M \rightarrow CF_3CF_2COCl + Cl + M$						
777	$CF_2ClCF_2CFClO + O_2 \rightarrow$ products	See data sheet					
777	$CF_2ClCF_2CFClO + M \rightarrow CF_2ClCF_2COF + Cl + M$						
777	$CH_2ClO + O_2 \rightarrow HCOCl + HO_2$	See data sheet					
777	$CH_2ClO + M \rightarrow HCO + HCl + M$						
777	$CH_3CHClO + O_2 \rightarrow CH_3COCl + HO_2$	See data sheet					
777	$CH_3CHClO + M \rightarrow CH_3CO + HCl + M$						
777	$HOCH_2CHClO + O_2 \rightarrow HOCH_2COCl + HO_2$	See data sheet					
777	$HOCH_2CHClO + M \rightarrow CH_2OH + HCOCl + M$						
777	$HOCHClCH_2O + O_2 \rightarrow HOCHClCHO + HO_2$	See data sheet					
777	$HOCHClCH_2O + M \rightarrow CHClOH + HCHO + M$						
777	$CH_3CCl_2O + O_2 \rightarrow$ products	See data sheet					
777	$CH_3CCl_2O + M \rightarrow CH_3COCl + Cl + M$						
777	$CCl_3CH_2O + O_2 \rightarrow CCl_3CHO + HO_2$	See data sheet					
777	$CCl_3CH_2O + M \rightarrow CCl_3 + HCHO + M$						
777	$CCl_3CCl_2O + O_2 \rightarrow$ products	See data sheet					
777	$CCl_3CCl_2O + M \rightarrow CCl_3COCl + Cl + M$						
781	$CH_2ClO_2 + NO \rightarrow CH_2ClO + NO_2$	1.9×10^{-11}		±0.3			
781	$CF_2ClO_2 + NO \rightarrow CF_2ClO + NO_2$	1.5×10^{-11}		±0.2	$1.5\times10^{-11}(T/298)^{-1.5}$	230–430	$\Delta\log k=\pm0.2$

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/ K
781	$CFCl_2O_2 + NO \rightarrow CFCl_2O + NO_2$	1.5×10^{-11}		±0.2	$1.5\times10^{-11}(T/298)^{-1.3}$	230–430	$\Delta\log k=\pm0.2$
781	$CCl_3O_2 + NO \rightarrow CCl_3O + NO_2$	1.8×10^{-11}		±0.2	$1.8\times10^{-11}(T/298)^{-1.0}$	230–430	$\Delta\log k=\pm0.2$
781	$CF_2ClCH_2O_2 + NO \rightarrow CF_2ClCH_2O + NO_2$	1.2×10^{-11}		±0.3			
781	$CFCl_2CH_2O_2 + NO \rightarrow CFCl_2CH_2O + NO_2$	1.3×10^{-11}		±0.3			
781	$CF_3CCl_2O_2 + NO \rightarrow CF_3CCl_2O + NO_2$	1.8×10^{-11}		±0.3			
882	$CF_2ClO_2 + NO_2 + M \rightarrow CF_2ClO_2NO_2 + M$	1.4×10^{-28} [N_2]	(k_0)	±0.5	$1.4\times10^{-28}(T/300)^{-6.4}$ [N_2]	200–300	$\Delta n=\pm2$
		7.5×10^{-12}	(k_∞)	±0.3	7.5×10^{-12}	200–300	$\Delta\log k=\pm0.3$
		$F_c=0.26$			$F_c=0.26$	220–300	
882	$CF_2ClO_2NO_2 + M \rightarrow CF_2ClO_2 + NO_2 + M$	9.0×10^{-19} [N_2]	(k_0/s^{-1})	±0.3	$1.8\times10^{-3}\exp(-10500/T)$ [N_2]	260–300	±500
		5.4×10^{-2}	(k_∞/s^{-1})	±0.3	$1.6\times10^{16}\exp(-11990/T)$	260–300	±500
		$F_c=0.26$			$F_c=0.26$	250–300	
883	$CFCl_2O_2 + NO_2 + M \rightarrow CFCl_2O_2NO_2 + M$	1.7×10^{-28} [N_2]	(k_0)	±0.3	$1.7\times10^{-28}(T/300)^{-6.7}$ [N_2]	230–300	$\Delta n=\pm2$
		7.5×10^{-12}	(k_∞)	±0.3	7.5×10^{-12}	250–300	$\Delta\log k=\pm0.3$
		$F_c=0.23$			$F_c=0.23$	230–300	
884	$CFCl_2O_2NO_2 + M \rightarrow CFCl_2O_2 + NO_2 + M$	1.5×10^{-18} [N_2]	(k_0/s^{-1})	±0.3	$1.0\times10^{-2}\exp(-10860/T)$	250–300	±500
		9.6×10^{-2}	(k_∞/s^{-1})	±0.3	$6.6\times10^{16}\exp(-12240/T)$	250–300	±500
		$F_c=0.23$			$F_c=0.23$	250–300	
884	$CCl_3O_2 + NO_2 + M \rightarrow CCl_3O_2NO_2 + M$	3.2×10^{-28} [N_2]	(k_0)	±0.5	$3.2\times10^{-28}(T/300)^{-7.7}$ [N_2]	230–300	$\Delta n=\pm3$
		7.5×10^{-12}	(k_∞)	±0.3	7.5×10^{-12}	250–300	$\Delta\log k=\pm0.3$
		$F_c=0.21$			$F_c=0.21$	250–300	
885	$CCl_3O_2NO_2 + M \rightarrow CCl_3O_2 + NO_2 + M$	7.6×10^{-18} [N_2]	(k_0/s^{-1})	±0.3	$6.3\times10^{-3}\exp(-10235/T)$ [N_2]	250–300	±500
		0.29	(k_∞/s^{-1})	±0.3	$4.8\times10^{16}\exp(-1820/T)$	250–300	±500
		$F_c=0.20$			$F_c=0.20$	250–300	
886	$C_2H5O_2 + CF_3CCl_2O_2$						
	$\rightarrow CH_3CHO + CF_3CCl_2OH + O_2$	3.6×10^{-12}		±0.3			
	$\rightarrow C_2H_5O + CF_3CCl_2O + O_2$	9×10^{-13}		±0.5			
886	$CF_2ClCH_2O_2 + CF_2ClCH_2O_2$						
	$\left.\begin{array}{l}\rightarrow CF_2ClCH_2OH + CF_2ClCHO + O_2\\ \rightarrow 2CF_2ClCH_2O + O_2\end{array}\right\}$	$\leq4\times10^{-12}$					
887	$CFCl_2CH_2O_2 + CFCl_2CH_2O_2$						
	$\left.\begin{array}{l}\rightarrow CFCl_2CH_2OH + CFCl_2CHO + O_2\\ \rightarrow 2CFCl_2CHO + O_2\end{array}\right\}$	$\leq4\times10^{-12}$					
887	$CF_3CCl_2O_2 + CF_3CCl_2O_2$						
	$\left.\begin{array}{l}\rightarrow CF_3CCl_2OOCCl_2CF_3 + O_2\\ \rightarrow 2CF_3CCl_2O + O_2\end{array}\right\}$	$\leq3\times10^{-12}$					
888	$CH_2ClO_2 + CH_2ClO_2 \rightarrow 2CH_2ClO + O_2$	3.7×10^{-12}		±0.2	$2.0\times10^{-13}\exp(870/T)$	250–600	±200
889	$\left.\begin{array}{l}CCl_3O_2 + CCl_3O_2 \rightarrow CCl_3OOCCl_3 + O_2\\ \qquad\qquad\qquad \rightarrow 2CCl_3O + O_2\end{array}\right\}$	1.6×10^{-12}		±0.3	$8.9\times10^{-14}\exp(860/T)$	250–430	±300
890	$CH_3CHClO_2 + CH_3CHClO_2$						
	$\left.\begin{array}{l}\rightarrow CH_3CHClOH + CH_3COCl + O_2\\ \rightarrow 2CH_3CHClO + O_2\end{array}\right\}$	5×10^{-12}		±0.3			
891	$CH_2ClCH_2O_2 + CH_2ClCH_2O_2$						
	$\left.\begin{array}{l}\rightarrow CH_2ClCH_2OH + CH_2ClCHO + O_2\\ \rightarrow 2CH_2ClCH_2O + O_2\end{array}\right\}$	$\leq4.8\times10^{-12}$			$\leq1.6\times10^{-13}\exp(1020/T)$	220–380	
892	$O_3 + C_2HCl_3 \rightarrow$ products	$<5\times10^{-20}$					
892	$O_3 + C_2Cl_4 \rightarrow$ products	$<10^{-21}$					

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/ K
892	$HCl + h\nu \rightarrow$ products	See data sheet					
893	$HOCl + h\nu \rightarrow$ products	See data sheet					
894	$OClO + h\nu \rightarrow$ products	See data sheet					
895	$Cl_2O + h\nu \rightarrow$ products	See data sheet					
895	$Cl_2O_2 + h\nu \rightarrow$ products	See data sheet					
896	$Cl_2O_3 + h\nu \rightarrow$ products	See data sheet					
897	$ClNO + h\nu \rightarrow$ products	See data sheet					
898	$ClONO + h\nu \rightarrow$ products	See data sheet					
898	$ClNO_2 + h\nu \rightarrow$ products	See data sheet					
899	$ClONO_2 + h\nu \rightarrow$ products	See data sheet					
900	$Cl_2 + h\nu \rightarrow$ products	See data sheet					
901	$CH_3Cl + h\nu \rightarrow$ products	See data sheet					
901	$CHF_2Cl + h\nu \rightarrow$ products	See data sheet					
902	$CF_2Cl_2 + h\nu \rightarrow$ products	See data sheet					
902	$CFCl_3 + h\nu \rightarrow$ products	See data sheet					
903	$CCl_4 + h\nu \rightarrow$ products	See data sheet					
904	$CH_3CF_2Cl + h\nu \rightarrow$ products	See data sheet					
905	$CH_3CFCl_2 + h\nu \rightarrow$ products	See data sheet					
905	$CH_3CCl_3 + h\nu \rightarrow$ products	See data sheet					
906	$CF_3CHFCl + h\nu \rightarrow$ products	See data sheet					
907	$CF_3CHCl_2 + h\nu \rightarrow$ products	See data sheet					
907	$CF_2ClCFCl_2 + h\nu \rightarrow$ products	See data sheet					
908	$CF_2ClCF_2Cl + h\nu \rightarrow$ products	See data sheet					
908	$CF_3CF_2Cl + h\nu \rightarrow$ products	See data sheet					
909	$CF_3CF_2CHCl_2 + h\nu \rightarrow$ products	See data sheet					
909	$CF_2ClCF_2CHFCl + h\nu \rightarrow$ products	See data sheet					
910	$HCOCl + h\nu \rightarrow$ products	See data sheet					
910	$COFCl + h\nu \rightarrow$ products	See data sheet					
911	$COCl_2 + h\nu \rightarrow$ products	See data sheet					
912	$CF_2ClCHO + h\nu \rightarrow$ products	See data sheet					
913	$CFCl_2CHO + h\nu \rightarrow$ products	See data sheet					
914	$CCl_3CHO + h\nu \rightarrow$ products	See data sheet					
916	$CF_3COCl + h\nu \rightarrow$ products	See data sheet					
	BrO_x Reactions						
918	$O + HOBr \rightarrow HO + BrO$	2.5×10^{-11}		±0.5			
918	$O + BrO \rightarrow O_2 + Br$	4.1×10^{-11}		±0.2	$1.9\times10^{-11}\exp(230/T)$	230–330	±150
919	$Br + HO_2 \rightarrow HBr + O_2$	2.0×10^{-12}		±0.3	$1.4\times10^{-11}\exp(-590/T)$	260–390	±200
919	$\left.\begin{array}{l} Br + H_2O_2 \rightarrow HBr + HO_2 \\ \quad\rightarrow HOBr + HO \end{array}\right\}$	$<5\times10^{-16}$					
919	$Br + O_3 \rightarrow BrO + O_2$	1.2×10^{-12}		±0.08	$1.7\times10^{-11}\exp(-800/T)$	195–392	±200
920	$Br + NO_2 + M \rightarrow BrNO_2 + M$	4.2×10^{-31} [N_2]	(k_0)	±0.3	$4.2\times10^{-31}(T/300)^{-2.4}$ [N_2]	200–300	$\Delta n=\pm1$
		2.7×10^{-11}	(k_∞)	±0.4	2.7×10^{-11}	200–300	$\Delta\log k=\pm0.4$
		$F_c=0.55$					

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
920	$Br + OClO \rightarrow BrO + ClO$	3.4×10^{-13}		±0.3	$2.6\times10^{-11}\exp(-1300/T)$	200–450	±300
921	$Br + Cl_2O \rightarrow BrCl + ClO$	4.3×10^{-12}		±0.1	$2.1\times10^{-11}\exp(-470/T)$	220–400	±200
921	$Br + Cl_2O_2 \rightarrow BrCl + ClOO$	3.0×10^{-12}		±0.3			
922	$Br + HCHO \rightarrow HBr + HCO$	1.1×10^{-12}		±0.15	$1.7\times10^{-11}\exp(-800/T)$	223–480	±250
922	$Br + CH_3CHO \rightarrow HBr + CH_3CO$	3.9×10^{-12}		±0.2	$1.3\times10^{-11}\exp(-360/T)$	250–400	±200
923	$HO + HBr \rightarrow H_2O + Br$	1.1×10^{-11}		±0.10	$1.1\times10^{-11}(T/298)^{-0.8}$	200–400	$\Delta n = ^{+0.8}_{-0.2}$
923	$HO + Br_2 \rightarrow HOBr + Br$	4.5×10^{-11}		±0.15	$1.2\times10^{-11}\exp(400/T)$	260–360	±400
924	$HO + CH_3Br \rightarrow H_2O + CH_2Br$	2.9×10^{-14}		±0.08	$1.7\times10^{-12}\exp(-1215/T)$	240–300	±150
925	$HO + CH_2Br_2 \rightarrow H_2O + CHBr_2$	1.1×10^{-13}		±0.20	$1.5\times10^{-12}\exp(-775/T)$	240–300	±300
926	$HO + CHF_2Br \rightarrow H_2O + CF_2Br$	9.8×10^{-15}		±0.10	$8.1\times10^{-13}\exp(-1315/T)$	240–300	±150
927	$HO + CF_3Br \rightarrow$ products	$<1\times10^{-16}$					
927	$HO + CF_2ClBr \rightarrow$ products	$<1\times10^{-16}$					
927	$HO + CF_2Br_2 \rightarrow$ products	$<5\times10^{-16}$					
928	$HO + CF_3CH_2Br \rightarrow H_2O + CF_3CHBr$	1.6×10^{-14}		±0.20	$1.4\times10^{-12}\exp(-1335/T)$	280–460	±300
928	$HO + CF_3CHFBr \rightarrow H_2O + CF_3CFBr$	1.7×10^{-14}		±0.2	$8.1\times10^{-13}\exp(-1155/T)$	279–460	±300
929	$HO + CF_3CHClBr \rightarrow H_2O + CF_3CClBr$	4.6×10^{-14}		±0.20	$1.2\times10^{-12}\exp(-970/T)$	298–460	±300
929	$HO + CF_2BrCF_2Br \rightarrow$ products	$<1.3\times10^{-16}$					
930	$Br + NO_3 \rightarrow BrO + NO_2$	1.6×10^{-11}		±0.3			
930	$BrO + NO_3 \rightarrow BrOO + NO_2$	1.0×10^{-12}		±0.5			
931	$NO_3 + HBr \rightarrow HNO_3 + Br$	$<1\times10^{-16}$					
932	$BrO + HO_2 \rightarrow HOBr + O_2$ $\rightarrow HBr + O_3$	3.3×10^{-11}		±0.2	$6.2\times10^{-12}\exp(500/T)$	200–300	±500
932	$BrO + O_3 \rightarrow Br + 2O_2$	$<5\times10^{-17}$					
933	$BrO + NO \rightarrow Br + NO_2$	2.1×10^{-11}		±0.1	$8.7\times10^{-12}\exp(260/T)$	224–425	±100
934	$BrO + NO_2 + M \rightarrow BrONO_2 + M$	4.7×10^{-31} [N_2]	(k_0)	±0.1	$4.7\times10^{-31}(T/300)^{-3.1}$ [N_2]	200–300	$\Delta n=\pm1$
		1.7×10^{-11}	(k_∞)	±0.1	$1.7\times10^{-11}(T/300)^{-0.6}$	200–300	$\Delta n=\pm1$
		$F_c=0.40$			$F_c=\exp(-T/327)$	200–300	
935	$BrO + ClO \rightarrow Br + OClO$	6.8×10^{-12}		±0.1	$1.6\times10^{-12}\exp(430/T)$	220–400	±200
	$\rightarrow Br + ClOO$	6.1×10^{-12}		±0.1	$2.9\times10^{-12}\exp(220/T)$	220–400	±200
	$\rightarrow BrCl + O_2$	1.0×10^{-12}		±0.1	$5.8\times10^{-13}\exp(170/T)$	220–400	±200
936	$BrO + BrO \rightarrow 2Br + O_2$	2.1×10^{-12}		±0.1	$4.0\times10^{-12}\exp(-190/T)$	220–400	±150
	$\rightarrow Br_2 + O_2$	3.8×10^{-13}		±0.1	$4.2\times10^{-14}\exp(660/T)$	220–400	±300
781	$CH_2BrO_2 + NO \rightarrow CH_2BrO + NO_2$	1.1×10^{-11}		±0.3			
937	$CH_2BrO_2 + CH_2BrO_2$ $\rightarrow CH_2BrOOCH_2Br + O_2$ $\rightarrow 2CH_2BrO + O_2$	$\leqslant3.3\times10^{-11}$					
938	$BrCH_2CH_2O_2 + BrCH_2CH_2O_2$						
	$\rightarrow BrCH_2CH_2OH + BrCH_2CHO + O_2$	1.6×10^{-12}		±0.3			
	$\rightarrow 2BrCH_2CH_2O + O_2$	2.3×10^{-12}		±0.3			
939	$BrO + CH_3SCH_3 \rightarrow$ products	$<2.7\times10^{-13}$					
939	$HOBr + h\nu \rightarrow$ products	See data sheet					
940	$BrO + h\nu \rightarrow$ products	See data sheet					
941	$BrONO_2 + h\nu \rightarrow$ products	See data sheet					
942	$CH_3Br + h\nu \rightarrow$ products	See data sheet					
943	$CF_3Br + h\nu \rightarrow$ products	See data sheet					

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	Δlog k_{298}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
943	$CF_2ClBr + h\nu \rightarrow$ products	See data sheet				
944	$CF_2Br_2 + h\nu \rightarrow$ products	See data sheet				
945	$CHBr_3 + h\nu \rightarrow$ products	See data sheet				
946	$CF_2BrCF_2Br + h\nu \rightarrow$ products	See data sheet				
	IO Reactions					
948	$O + I_2 \rightarrow IO + I$	1.4×10^{-10}	±0.3	1.4×10^{-10}	200–400	±250
948	$O + IO \rightarrow O_2 + I$	3×10^{-11}	±0.5			
948	$I + HO_2 \rightarrow HI + O_2$	3.8×10^{-13}	±0.3	$1.5\times10^{-11}\exp(-1090/T)$	250–350	±500
949	$I + O_3 \rightarrow IO + O_2$	1.0×10^{-12}	±0.2	$2.0\times10^{-11}\exp(-890/T)$	200–350	±300
949	$I + NO + M \rightarrow INO + M$	1.8×10^{-32} [N$_2$] (k_0)	±0.1	$1.8\times10^{-32}(T/300)^{-1.0}$ [N$_2$]	200–400	$\Delta n=\pm0.5$
		1.7×10^{-11} (k_∞)	±0.3	1.7×10^{-11}	200–400	$\Delta n=\pm0.5$
		$F_c=0.75$		$F_c=[\exp(-T/1040)+\exp(-4160/T)]$	200–400	
949	$I + NO_2 + M \rightarrow INO_2 + M$	3.0×10^{-31} [N$_2$] (k_0)	±0.2	$3.0\times10^{-31}(T/300)^{-1}$ [N$_2$]	200–400	$\Delta n=\pm1$
		6.6×10^{-11} (k_∞)	±0.3	6.6×10^{-11}	200–400	$\Delta\log k=\pm0.3$
		$F_c=0.63$		$F_c=[\exp(-T/650)+\exp(-2600/T)]$	200–400	
950	$I + NO_3 \rightarrow IO + NO_2$	No recommendation (see data sheet)				
951	$I_2 + NO_3 \rightarrow I + IONO_2$	1.5×10^{-12}	±0.3			
951	$HO + HI \rightarrow H_2O + I$	3.0×10^{-11}	±0.3			
951	$HO + I_2 \rightarrow HOI + I$	1.8×10^{-10}	±0.3			
952	$HO + CH_3I \rightarrow H_2O + CH_2I$	7.2×10^{-14}	±0.5	$3.1\times10^{-12}\exp(-1120/T)$	270–430	±500
952	$HO + CF_3I \rightarrow$ products	$<4\times10^{-14}$				
953	$NO_3 + HI \rightarrow HNO_3 + I$	No recommendation (see data sheet)				
953	$IO + HO_2 \rightarrow HOI + O_2$	1.0×10^{-10}	±0.3			
954	$IO + IO \rightarrow$ products	5.2×10^{-11}	±0.3	$1.7\times10^{-12}\exp(1020/T)$	250–373	±500
954	$IO + NO \rightarrow I + NO_2$	2.2×10^{-11}	±0.3	$7.3\times10^{-12}\exp(330/T)$	200–400	±150
955	$IO + NO_2 + M \rightarrow IONO_2 + M$	7.7×10^{-31} [N$_2$] (k_0)	±0.3	$7.7\times10^{-31}(T/300)^{-5}$ [N$_2$]	250–350	$\Delta n=\pm2$
		1.6×10^{-11} (k_∞)	±0.3	1.6×10^{-11}	250–350	$\Delta\log k=\pm0.3$
		$F_c=0.4$				
956	$IO + CH_3SCH_3 \rightarrow$ products	1.2×10^{-14}	±0.5			
957	$INO + INO \rightarrow I_2 + 2NO$	1.3×10^{-14}	±0.4	$8.4\times10^{-11}\exp(-2620/T)$	300–450	±600
957	$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$	4.7×10^{-15}	±0.5	$2.9\times10^{-11}\exp(-2600/T)$	298–400	±1000
957	$CH_2IO_2 + CH_2IO_2 \rightarrow CH_2IOH + HCOI + O_2$ $\rightarrow 2CH_2IO + O_2$	No recommendation (see data sheet)				
958	$HOI + h\nu \rightarrow$ products	See data sheet				
958	$IO + h\nu \rightarrow$ products	See data sheet				
959	$INO + h\nu \rightarrow$ products	See data sheet				
960	$INO_2 + h\nu \rightarrow$ products	See data sheet				
960	$IONO_2 + h\nu \rightarrow$ products	See data sheet				
961	$CH_3I + h\nu \rightarrow$ products	See data sheet				
962	$CF_3I + h\nu \rightarrow$ products	See data sheet				

*See data sheets in IUPAC (1992) [J. Phys. Chem. Ref. Data **21**, 1125 (1992)].

TABLE 2. (b) Heterogeneous Reactions—Summary of Reactions.

Page Number	Reaction	
	Uptake Kinetics with Chemical Reaction	
964	$N_2O_5 + H_2O \rightarrow 2HNO_3$ (including uptake studies)	See data sheets
968	$N_2O_5 + HCl \rightarrow HNO_3 + NO_2Cl$	See data sheets
969	$N_2O_5 + HBr \rightarrow BrONO + HNO_3$	See data sheets
970	$N_2O_5 + NaCl \rightarrow ClNO_2 + NaNO_3$	See data sheets
971	$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$ (including uptake studies)	See data sheets
975	$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$	See data sheets
979	$ClONO_2 + HBr \rightarrow BrCl + HNO_3$	See data sheets
979	$ClONO_2 + HF \rightarrow$ products	See data sheets
980	$ClONO_2 + NaCl \rightarrow Cl_2 + NaNO_3$	See data sheets
980	$HOCl + HCl \rightarrow Cl_2 + H_2O$	See data sheets
982	$BrONO_2 + H_2O \rightarrow HOBr + HNO_3$	See data sheets
982	$BrONO_2 + HCl \rightarrow BrCl + HNO_3$	See data sheets
983	$HBr + Cl_2 \rightarrow HCl + BrCl$	See data sheets
983	$HOBr + HBr \rightarrow Br_2 + H_2O$	See data sheets
983	$HOBr + HCl \rightarrow BrCl + H_2O$	See data sheets
984	O_3 + Substrate (C_{am}) $\rightarrow$ products (O_2, CO, CO_2, $\{C_{am}O\}$)	See data sheets
984	$SO_2 + H_2O_2 \rightarrow H_2SO_4$	See data sheets
985	$COF_2 + H_2O \rightarrow 2HF + CO_2$	See data sheets
985	$COCl_2 + H_2O \rightarrow 2HCl + CO_2$	See data sheets
986	$CCl_3COCl + H_2O \rightarrow CCl_3COOH + HCl$	See data sheets
986	$CF_3COF + H_2O \rightarrow CF_3COOH + HF$	See data sheets
987	$CF_3COCl + H_2O \rightarrow CF_3COOH + HCl$	See data sheets
987	NO_2/N_2O_4 + Substrate (amorphous Carbon, NaCl) $\rightarrow$ products	See data sheets
	Uptake Kinetics without Chemical Reaction	
988	HO_2 + Substrate (SiO_2, H_2O aerosol)	See data sheets
989	OH + Substrate (H_2O, SiO_2, H_2SO_4)	See data sheets
990	H_2O + Substrate (water ice, NAT, NaCl)	See data sheets
991	HCl + Substrate (water ice, NAT, H_2SO_4/H_2O, NaCl)	See data sheets
993	$HOCl$ + Substrate (water ice)	See data sheets
994	HBr + Substrate (water ice, NAT)	See data sheets
994	$HOBr$ + Substrate (Pyrex, water ice, H_2SO_4/H_2O)	See data sheets
995	HNO_3 + Substrate (water ice, water droplets, H_2SO_4/H_2O, salt surfaces)	See data sheets
997	$HONO$ + Substrate (water droplets and liquid jet)	See data sheets
998	NO + Substrate (water ice, 70% H_2SO_4-H_2O-ice)	See data sheets
999	NO_2 + Substrate (water ice and droplets, 70% H_2SO_4-H_2O-ice)	See data sheets
999	$CH_3CO(O)_2NO_2$ (PAN) + Substrate (water jet)	See data sheets
1000	NH_3 + Substrate (liquid water jet, water droplets)	See data sheets
1000	O_3 + Substrate (water ice, liquid, NAT, Pyrex)	See data sheets
1001	Cl_2 + Substrate (water ice)	See data sheets
1001	ClO + Substrate (water ice, H_2SO_4-H_2O, NAT, Pyrex)	See data sheets
1002	Cl + Substrate (SiO_2, H_2SO_4-H_2O, Teflon)	See data sheets
1003	Br + Substrate (Teflon)	See data sheets
1003	SO_2 + Substrate (water droplets and jet)	See data sheets
1004	H_2O_2 + Substrate (water droplets)	See data sheets
1005	CH_3COCH_3 + Substrate (water droplets)	See data sheets
1005	H_2CO + Substrate (water droplets, H_2SO_4/H_2O solution)	See data sheets
1006	CH_3CHO + Substrate (water droplets)	See data sheets
1006	$CHBr_3$ + Substrate (water ice, H_2SO_4)	See data sheets
1006	CH_3OH + Substrate (water droplets)	See data sheets
1006	C_2H_5OH + Substrate (water droplets)	See data sheets
1006	1-C_3H_7OH + Substrate (water droplets)	See data sheets
1006	2-C_3H_7OH + Substrate (water droplets)	See data sheets
1006	$CH_3C(CH_3)(OH)CH_3$ + Substrate (water droplets)	See data sheets
1006	$ClCH_2CH_2OH$ + Substrate (water droplets)	See data sheets
1006	$BrCH_2CH_2OH$ + Substrate (water droplets)	See data sheets
1006	ICH_2CH_2OH + Substrate (water droplets)	See data sheets
1006	$HOCH_2CH_2OH$ + Substrate (water droplets)	See data sheets
1007	$HCOOH$ + Substrate (water droplets)	See data sheets
1007	CH_3COOH + Substrate (water droplets)	See data sheets
1008	CCl_3COOH + Substrate (water droplets)	See data sheets
1008	CCl_2HCOOH + Substrate (water droplets)	See data sheets
1008	$CClH_2COOH$ + Substrate (water droplets)	See data sheets
1008	$CF_2ClCOOH$ + Substrate (water droplets)	See data sheets
1008	CF_3COOH + Substrate (water droplets)	See data sheets

3. Guide to the Data Sheets

3.1. Gas-Phase Reactions

The data sheets are principally of two types: (i) those for individual thermal reactions and (ii) those for the individual photochemical reactions. We also include a few composite data sheets consisting of a group of analogous reactions usually studied by a common technique.

3.1.1. Thermal Reactions

The data sheets begin with a statement of the reactions including all pathways which are considered feasible. This is followed by the corresponding enthalpy changes at 298 K, calculated from the enthalpies of formation summarized in Appendix 1.

The available kinetic data on the reactions are summarized under three headings: (i) absolute rate coefficients, (ii) relative rate coefficients, and (iii) reviews and evaluations. Under headings (i) and (ii), we list new data which have been published since the last IUPAC evaluation.[5] Under heading (iii) are listed the preferred rate data from the most recently published NASA evaluation available at the date of submission of this evaluation and our own IUPAC evaluations, together with data from any new review or evaluation source. Under all three of the headings above, the data are presented as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in a temperature-dependent form over a stated range of temperatures. For bimolecular reactions, the temperature dependence is usually expressed in the normal Arrhenius form, $k=A\ \exp(-B/T)$, where $B=E/R$. For a few bimolecular reactions, we have listed temperature dependences in the alternative form, $k=A'T^{-n}$ or $CT^{n}\ \exp(-D/T)$, where the original authors have found this to give a better fit to their data. For pressure-dependent combination and dissociation reactions, the non-Arrhenius temperature dependence is used. This is discussed more fully in a subsequent section of the Introduction.

Single temperature data are presented as such and wherever possible the rate coefficient at, or close to, 298 K is quoted directly as measured by the original authors. This means that the listed rate coefficient at 298 K may differ slightly from that calculated from the Arrhenius parameters determined by the same authors. Rate coefficients at 298 K marked with an asterisk indicate that the value was calculated by extrapolation of a measured temperature range which did not include 298 K. The tables of data are supplemented by a series of comments summarizing the experimental details. The following list of abbreviations, relating to experimental techniques, is used mainly in the comments section:

EPR - electron paramagnetic resonance
FTIR - Fourier transform infrared
GC - gas chromatography/gas chromatographic
HPLC - high performance liquid chromatography
IR - infrared
LIF - laser induced fluorescence
LMR - laser magnetic resonance
MS - mass spectrometry/mass spectrometric
UV - ultraviolet

For measurements of relative rate coefficients, wherever possible the comments contain the actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient given in the table may be different from that reported by the original author owing to a different choice of rate coefficient of the reference reaction. Whenever possible the reference rate data are those preferred in the present evaluation.

The preferred rate coefficients are presented (i) at a temperature of 298 K and (ii) in temperature-dependent form over a stated range of temperatures.

This is followed by a statement of the error limits in log k at 298 K and the error limits either in (E/R) or in n, for the mean temperature in the range. Some comments on the assignment of errors are given later in this introduction.

The "Comments on Preferred Values" describe how the selection was made and give any other relevant information. The extent of the comments depends upon the present state of our knowledge of the particular reaction in question. The data sheets are concluded with a list of the relevant references.

3.1.2. Conventions Concerning Rate Coefficients

All of the reactions in the table are elementary processes. Thus the rate expression is derived from a statement of the reaction, e.g.,

$$\mathrm{A+A \rightarrow B+C}$$

$$\frac{-1/2\mathrm{d[A]}}{\mathrm{d}t}=\frac{\mathrm{d[B]}}{\mathrm{d}t}=\frac{\mathrm{d[C]}}{\mathrm{d}t}=k[\mathrm{A}]^2$$

Note that the stoichiometric coefficient for A, i.e., 2, appears in the denominator before the rate of change of [A] (which is equal to $2k[\mathrm{A}]^2$) and as a power on the right-hand side.

3.1.3. Treatment of Combination and Dissociation Reactions

The rates of combination and the reverse dissociation reactions

$$\mathrm{A+B+M \rightleftarrows AB+M}$$

depend on the temperature T, and the nature and concentration of the third body [M]. The rate coefficients of these reactions have to be expressed in a form which is more complicated than those for simple bimolecular reactions. The combination reactions are described by a pseudo second-order rate law

$$\frac{\mathrm{d[AB]}}{\mathrm{d}t}=k[\mathrm{A}][\mathrm{B}]$$

in which the second-order rate coefficient depends on [M]. The low-pressure third-order limit is characterized by k_0,

$$k_0 = \lim_{[\mathrm{M}]\to 0} k([\mathrm{M}])$$

which is proportional to [M]. The high-pressure second-order limit is characterized by k_∞,

$$k_\infty = \lim_{[\mathrm{M}]\to \infty} k([\mathrm{M}])$$

which is independent of [M]. For a combination reaction in the low-pressure range, the summary table gives a second-order rate coefficient expressed as the product of a third-order rate coefficient and the third body concentration which is expressed in molecule cm^{-3}. The transition between the third-order and the second-order range is represented by a reduced falloff expression of k_0/k_∞ as a function of

$$k_0/k_\infty = [\mathrm{M}]/[\mathrm{M}]_c,$$

where the "center of the falloff curve" $[\mathrm{M}]_c$ indicates the third-body concentration for which the extrapolated k_0 would be equal to k_∞. The dependence of k on [M] in general is complicated and has to be analyzed by unimolecular rate theory. For moderately complex molecules at not too high temperatures, however, a simple approximate relationship holds:

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty} F = k_0 \frac{1}{1 + k_0/k_\infty} F = k_\infty \frac{k_0/k_\infty}{1 + k_0/k_\infty} F,$$

where the first factors at the right-hand side represent the Lindemann-Hinshelwood expression, and the additional broadening factor F, at not too high temperature, is approximately given by[6–8]

$$\log F \cong \frac{\log F_c}{1 + [\log(k_0/k_\infty)]^2}.$$

With increasing temperature, a better representation is obtained[6–8] by replacing $[\log(k_0/k_\infty)]^2$ by $[\log(k_0/k_\infty)/\mathrm{N}]^2$ with $\mathrm{N} = \{0.75 - 1.27 \log F_c\}$. In this way the three quantities k_0, k_∞, and F_c characterize the falloff curve for the present application.

Alternatively, the three quantities k_∞, $[\mathrm{M}]_c$, and F_c (or k_0, $[\mathrm{M}]_c$, and F_c) can be used. The temperature dependence of F_c, which is sometimes significant, can be estimated by the procedure of Troe.[7–9] The results can usually be represented[9] approximately by an equation

$$F_c = (1 - a)\exp(-T/T^{***}) + a \exp(-T/T^{*}) + \exp(-T^{**}/T).$$

Whereas the two first terms are of importance for atmospheric conditions, the last term in most cases becomes relevant only at much higher temperatures. In Ref. 2, for simplicity $a = 1$ and $T^{**} = 4T^{*}$ was adopted. Often $F_c = \exp(-T/T^{*})$ is sufficient for low temperature conditions. With molecules of increasing complexity, additional broadening of the falloff curves may have to be taken into account.[7–9] For simplicity these effects are neglected in the present evaluation. An even simpler policy was chosen in Ref. 6 where a temperature independent standard value of $F_c = 0.6$ was adopted.

Changes in F_c would require changes in the limiting k_0 and k_∞ values. For the purpose of this evaluation, this will be irrelevant in most cases, if the preferred k_0 and k_∞ are used consistently together with the preferred F_c values. If the selected value of F_c is too large, the values of k_0 and k_∞, obtained by fitting the falloff expression to the experimental data, are underestimated.

Theoretical predictions of F_c have been derived from rigid RRKM-type models including weak collision effects.[7–9]

The dependence of k_0 and k_∞ on the temperature T is represented in the form:

$$k \propto T^{-n}$$

(except for the cases with an established energy barrier in the potential). We have used this form of temperature dependence because it often gives a better fit to the data over a wider range of temperature than does the Arrhenius expression. The dependence of k_0 on the nature of the third-body M generally is represented by the relative efficiencies of M_1 and M_2.

$$k_0(\mathrm{M}_1)/[\mathrm{M}_1] : k_0(\mathrm{M}_2)/[\mathrm{M}_2]$$

The few thermal dissociation reactions of interest in the present application are treated by analogy with combination reactions, with pseudo-first-order rate coefficients $k([\mathrm{M}])$. The limiting low- and high-pressure rate coefficients expressed in units of s^{-1} are denoted in the tables by the symbols (k_0/s^{-1}) and $(k_\infty/\mathrm{s}^{-1})$. F_c is the same in combination and dissociation reactions.

3.1.4. Photochemical Reactions

The data sheets begin with a list of feasible primary photochemical transitions for wavelengths usually down to 170 nm, along with the corresponding enthalpy changes at 0 K where possible or alternatively at 298 K, calculated from the data in Appendix 1. Calculated threshold wavelengths corresponding to these enthalpy changes are also listed, bearing in mind that the values calculated from the enthalpy changes at 298 K are not true "threshold values."

This is followed by tables summarizing the available experimental data on (i) absorption cross-sections and (ii) quantum yields. These data are supplemented by a series of comments.

The next table lists the preferred absorption cross-section data and the preferred quantum yields at appropriate wavelength intervals. For absorption cross-sections the intervals are usually 1, 5, or 10 nm. Any temperature dependence of the absorption cross-sections is also given where possible. The aim in presenting these preferred data is to provide a basis for calculating atmospheric photolysis rates. For absorption continua the temperature dependence is often represented by Sulzer-Wieland type expressions.[10]

The comments again describe how the preferred data were selected and include other relevant points. The photochemical data sheets are also concluded with a list of references.

In this evaluation we have provided data sheets for all of the photochemical reactions listed in the Summary Table and not just those for which new data have become available since our last evaluation.

3.1.5. Conventions Concerning Absorption Cross-Sections

These are presented in the data sheets as "absorption cross-sections per molecule, base e." They are defined according to the equations

$$I/I_0=\exp(-\sigma[N]l),$$

$$\sigma=\{1/([N]l)\}\ln(I_0/I),$$

where I_0 and I are the incident and transmitted light intensities, σ is the absorption cross-section per molecule (expressed in this paper in units of cm^2), [N] is the number concentration of absorber (expressed in molecule cm^{-3}), and l is the path length (expressed in cm). Other definitions and units are frequently quoted. The closely related quantities "absorption coefficient" and "extinction coefficient" are often used, but care must be taken to avoid confusion in their definition; it is always necessary to know the units of concentration and of path length and the type of logarithm (base e or base 10) corresponding to the definition. To convert an absorption cross-section to the equivalent Naperian (base e) absorption coefficient of a gas at a pressure of one standard atmosphere and temperature of 273 K (expressed in cm^{-1}), multiply the value of σ in cm^2 by 2.69×10^{19}.

3.1.6. Assignment of Errors

Under the heading "reliability," estimates have been made of the absolute accuracies of the preferred values of k at 298 K and of the preferred values of E/R over the quoted temperature range. The accuracy of the preferred rate coefficient at 298 K is quoted as the term $\Delta\log k$, where $\Delta\log k=D$ and D is defined by the equation, $\log_{10} k=C\pm D$. This is equivalent to the statement that k is uncertain to a factor of F, where $D=\log_{10}F$. The accuracy of the preferred value of E/R is quoted as the term $\Delta(E/R)$, where $\Delta(E/R)=G$ and G is defined by the equation $E/R=H\pm G$.

For second-order rate coefficients listed in this evaluation, an estimate of the uncertainty at any given temperature within the recommended temperature range may be obtained from the equation:

$$\Delta\log k(T)=\Delta\log k(298)+0.4343\exp\left|\frac{\Delta E}{R}\left(\frac{1}{T}-\frac{1}{298}\right)\right|$$

(note that the exponent in this equation is an absolute value).

The assignment of these absolute error limits in k and E/R is a subjective assessment of the evaluators. Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurement, i.e., the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 90% confidence limits, of ±10% or less are frequently reported in the literature. Unfortunately, when evaluators come to compare data for the same reaction studied by more than one group of investigators and involving different techniques, the rate coefficients often differ by a factor of 2 or even more. This can only mean that one or more of the studies has involved large systematic errors which are difficult to detect. This is hardly surprising since, unlike molecular reactions, it is not always possible to study atomic and free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise.

The arbitrary assignment of errors made here is based mainly on our state of knowledge of a particular reaction which is dependent upon factors such as the number of independent investigations made and the number of different techniques used. On the whole, our assessment of error limits errs towards the cautious side. Thus, in the case where a rate coefficient has been measured by a single investigation using one particular technique and is unconfirmed by independent work, we suggest that minimum error limits of a factor of 2 are appropriate.

In contrast with the usual situation for the rate coefficients of thermal reactions, where intercomparison of results of a number of independent studies permits a realistic assessment of reliability, for many photochemical processes there is a scarcity of apparent reliable data. Thus, we do not feel justified at present in assigning error limits to the parameters reported for the photochemical reactions.

3.2. Heterogeneous Reactions

The data sheets contain six columns listing (i) the type of uptake coefficient which has been measured, (ii) the value of the reported uptake coefficient with the observed error limits, (iii) the nature of the condensed phase with specific experimental conditions where appropriate, (iv) the temperature of the experiments, (v) the literature reference, and (vi) the reference to the **Comments** on the experimental techniques.

The Comments are written to enable the reader to obtain an impression of the experimental variables of the complex kinetic systems in question. These brief experimental descriptions are also intended to facilitate the comparison of results obtained using different kinetic techniques.

Where possible under the heading **Preferred Values** is given a summary of the conclusions we have reached regarding the values of the uptake coefficients for any given reaction.

In reviewing the literature on heterogeneous reactions relevant to atmospheric chemistry, we have disregarded some early work which is not in line with more recent findings as well as early work involving the same techniques on reactions for which no recent data are available.

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3.4. References to Sections 1 through 3

[1] CODATA Task Group on Chemical Kinetics, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data **9**, 295 (1980).

[2] CODATA Task Group on Chemical Kinetics, D. L. Baulch, R. A. Cox, P. J. Crutzen, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data **11**, 327 (1982).

[3] CODATA Task Group on Gas Phase Chemical Kinetics, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data **13**, 1259 (1984).

[4] IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, J. Phys. Chem. Ref. Data **18**, 881 (1989).

[5] IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, J. Phys. Chem. Ref. Data **21**, 1125 (1992).

[6] NASA Panel for Data Evaluation, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Evaluation Number 11, W. B. DeMore, S.P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C.J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, JPL Publication 94-26 (1994). (Contains references to the previous Evaluations, Numbers 1–10, in this series).

[7] J. Troe, J. Phys. Chem. **83**, 114 (1979).

[8] J. Troe, Ber. Bunsenges. Phys. Chem. **87**, 161 (1983).

[9] R. G. Gilbert, K. Luther, and J. Troe, Ber. Bunsenges. Phys. Chem. **87**, 169 (1983).

[10] D. C. Astholz, L. Brouwer, and J. Troe, Ber. Bunsenges. Phys. Chem. **85**, 559 (1981).

4. Gas-Phase Reactions—Data Sheets

4.1. Oxygen Species

$O + O_2 + M \rightarrow O_3 + M$

$\Delta H° = -106.5$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 5.6 \times 10^{-34} (T/300)^{-2.8} [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 100–300 K.

$k_0 = 6.0 \times 10^{-34} (T/300)^{-2.8} [O_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 100–300 K.

Reliability

$\Delta \log k_0 = \pm 0.05$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The results from Ref. 1, obtained over extended temperature ranges, confirm the large negative values of n and also confirm earlier absolute values of k_0 at 298 K. The value of n is probably similar for N_2 and O_2, as for the reaction $Cl + O_2 + M \rightarrow ClOO + M$ also studied at low temperatures (see this evaluation), and governed by a radical-complex mechanism. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[2]

Comments on High-pressure Rate Coefficients and Falloff Range

The experiments from Ref. 1 under low temperature and high pressure conditions indicate anomalous falloff behavior different from the formalism described in the Introduction. These effects are not relevant for atmospheric conditions such that they are not included in this evaluation.

References

[1] H. Hippler, R. Rahn, and J. Troe, J. Chem. Phys. **93**, 6560 (1990).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O + O_3 \rightarrow 2O_2$

$\Delta H° = -391.9$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 8.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.0 \times 10^{-12} \exp(-2060/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The study of Wine *et al.*[1] yields values of k in close agreement with those from other studies over the whole temperature range covered. Our recommendations are based on the least-squares expression obtained by Wine *et al.*[1] from a fit of their own data plus those of McCrumb and Kaufman,[2] Davis *et al.*,[3] West *et al.*[4] and Arnold and Comes.[5] The preferred values are identical to our previous evaluation, IUPAC, 1992.[6]

References

[1] P. H. Wine, J. M. Nicovich, R. J. Thompson, and A. R. Ravishankara, J. Phys. Chem. **87**, 3948 (1983).

[2] J. L. McCrumb and F. Kaufman, J. Chem. Phys. **57**, 1270 (1972).

[3] D. D. Davis, W. Wong, and J. Lephardt, Chem. Phys. Lett. **22**, 273 (1973).

[4] G. A. West, R. E. Weston, Jr., and G. W. Flynn, Chem. Phys. Lett. **56**, 429 (1978).

[5] I. Arnold and F. J. Comes, Chem. Phys. **42**, 231 (1979).

[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\begin{aligned} O(^1D) + O_2 &\rightarrow O(^3P) + O_2(^1\Sigma_g^+) \quad (1)\\ &\rightarrow O(^3P) + O_2(^1\Delta_g) \quad (2)\\ &\rightarrow O(^3P) + O_2(^3\Sigma_g^-) \quad (3)\end{aligned}$$

$\Delta H°(1) = -32.8$ kJ·mol^{-1}
$\Delta H°(2) = -95.4$ kJ·mol^{-1}
$\Delta H°(3) = -189.7$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

No new data have been published since our last evaluation.

Preferred Values

$k = 4.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.2 \times 10^{-11} \exp(67/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–350 K.
$k_1/k = 0.8$ at 298 K.
$k_2/k \leq 0.05$ at 298 K.

Reliability

$\Delta \log k = \pm 0.05$ at 298 K.
$\Delta(E/R) = \pm 100$ K.
$\Delta \log(k_1/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1982.[1] The earlier controversy between measurements using O(^{1}D) emission at 630 nm and absorption at 115 nm now appears to be resolved, since O(^{3}P) atom detection by absorption at 130 nm and fluorescence support the O(^{1}D) emission results. Apparently the γ-value in the Lambert-Beer law used for the O(^{1}D) absorption results was too small. The preferred 298 K rate coefficient is the average of the results from Amimoto *et al.*,[2] Brock and Watson,[3] Lee and Slanger,[4] and Streit *et al.*[5] The branching ratios of Lee and Slanger[4] and Gauthier and Snelling[6] are recommended. The preferred values are identical to our previous evaluation, IUPAC, 1992.[7]

References

[1] CODATA, Supplement I, 1982 (see references in Introduction).
[2] S. T. Amimoto, A. P. Force, R. G. Gulotty, Jr., and J. R. Wiesenfeld, J. Chem. Phys. **71**, 3640 (1979).
[3] J. C. Brock and R. T. Watson, Reported at the NATO Advanced Study Institute on Atmospheric Ozone, Portugal (1979). See also G. K. Moortgat in Report No. FAA-EE.80-20 (1980).
[4] L. C. Lee and T. G. Slanger, Geophys. Res. Lett. **6**, 165 (1979).
[5] G. E. Streit, C. J. Howard, A. L. Schmeltekopf, J. A. Davidson, and H. I. Schiff, J. Chem. Phys. **65**, 4761 (1976).
[6] M. Gauthier and D. R. Snelling, J. Chem. Phys. **54**, 4317 (1971).
[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\begin{aligned} O(^1D) + O_3 &\rightarrow O_2 + 2O(^3P) \quad (1)\\ &\rightarrow O(^3P) + O_3 \quad (2)\\ &\rightarrow 2O_2(^1\Delta_g) \quad (3)\\ &\rightarrow O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-) \quad (4)\\ &\rightarrow 2O_2(^3\Sigma_g^-) \quad (5)\end{aligned}$$

$\Delta H°(1) = -83.2$ kJ·mol^{-1}
$\Delta H°(2) = -189.7$ kJ·mol^{-1}
$\Delta H°(3) = -393.0$ kJ·mol^{-1}
$\Delta H°(4) = -424.7$ kJ·mol^{-1}
$\Delta H°(5) = -581.6$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

No new data have been published since our last evaluation.

Preferred Values

$k = 2.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 100–400 K.
$k_1/k = k_5/k = 0.5$ at 298 K.

Reliability

$\Delta \log k = \pm\ 0.05$ over the temperature range 100–400 K.
$\Delta \log k_1/k = \Delta \log k_5/k = \pm\ 0.1$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[1] The measurement of the rate coefficient k at 298 K by Greenblatt and Wiesenfeld[2] is in excellent agreement with our earlier recommendation.[3] The determination of k_1/k_5 by Cobos *et al.*[4] is rather indirect, but provides further evidence that $k_1 \approx k_5$. Our previous recommendations[1,3,5] are unchanged.

References

[1] CODATA, Supplement II, 1984 (see references in Introduction).
[2] G. D. Greenblatt and J. R. Wiesenfeld, J. Chem. Phys. **78**, 4924 (1983).
[3] CODATA, Supplement I, 1982 (see references in Introduction).
[4] C. Cobos, E. Castellano, and H. J. Schumacher, J. Photochem. **21**, 291 (1983).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O_2^* + O_3 \rightarrow O + 2O_2$

Comments

These comments are reproduced from our previous evaluation, IUPAC, 1992.[1] Arnold and Comes[2,3] have studied this reaction of vibrationally excited oxygen molecules in the ground electronic state with ozone and they report a rate coefficient of 2.8×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K. The vibrationally excited oxygen molecules were produced in the reaction of O(^{1}D) atoms with O_3 following the UV photolysis of ozone. This is the only reported study of this rate coefficient, and we make no recommendation. For further discussion the reader is referred to the review by Steinfeld *et al.*[4]

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).
[2] I. Arnold and F. J. Comes, Chem. Phys. **47**, 125 (1980).
[3] I. Arnold and F. J. Comes, J. Mol. Struct. **61**, 223 (1980).
[4] J. I. Steinfeld, S. M. Adler-Golden, and J. W. Gallagher, J. Phys. Chem Ref. Data **16**, 911 (1987).

$O_2(^3\Sigma_g^-, v) + M \rightarrow O_2(^3\Sigma_g^-, v') + M$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	M	v	Temp./K	Reference	Comment
Absolute Rate Coefficients					
$(4.7\pm0.3)\times10^{-15}$	O_2	19	295	Price *et al.*, 1993[1]	(a)
$(3.2\pm0.3)\times10^{-15}$		20			
$(5.8\pm1.2)\times10^{-15}$		21			
$(5.4\pm0.8)\times10^{-14}$		22			
$(1.2\pm0.4)\times10^{-14}$		23			
$(0.84\pm0.04)\times10^{-14}$		24			
$(1.8\pm0.05)\times10^{-14}$		25			
$(4.7\pm0.2)\times10^{-14}$		26			
$(2.3\pm0.1)\times10^{-14}$	O_2	19	460		
$(3.1\pm0.08)\times10^{-14}$		20			
$(2.2\pm0.9)\times10^{-14}$		21			
$(3.7\pm0.3)\times10^{-14}$		22			
$(4.1\pm0.6)\times10^{-14}$		23			
$(6.9\pm0.5)\times10^{-14}$		24			
$(11.7\pm0.2)\times10^{-14}$		25			
$(16.4\pm2)\times10^{-14}$		26			
$>8.3\times10^{-14}$		27			
$>1.2\times10^{-11}$		28			
6.5×10^{-14}	O_2	8	300	Park and Slanger, 1994[2]	(b)
$>1.3\times10^{-13}$	He	22			
$(1.53\pm0.25)\times10^{-11}$	O_3	22			
2×10^{-13}	CO_2	14			
9×10^{-14}		22			

Comments

(a) Vibrationally highly excited electronic ground state O_2 molecules were generated by stimulated emission pumping, and detected by LIF.

(b) Vibrationally highly excited electronic ground state O_2 molecules were formed by ozone photodissociati at 248 nm (Hartley band). The excited molecules we detected by LIF. Rate coefficients were evaluated usi a cascade model, in which relaxation through sing quantum V-V and V-T steps was assumed.

Preferred Values

See table.

Reliability
$\Delta \log k = \pm 0.5$.

Comments on Preferred Values
The results given from Ref. 1 and more results presented in graphical form from Ref. 2 appear consistent with each other.

References

[1] J. M. Price, J. A. Mack, C. A. Rogaski, and A. M. Wodtke, Chem. Phys. **175**, 83 (1993).
[2] H. Park and T. G. Slanger, J. Chem. Phys. **100**, 287 (1994).

$O_2(^1\Delta_g) + M \rightarrow O_2(^3\Sigma_g^-) + M$

$\Delta H^\circ = -94.3$ kJ·mol^{-1}

Rate Coefficient Data

No new data have been published since our last evaluation.

Preferred Values

$k = 1.6\times10^{-18}$ cm^3 molecule^{-1} s^{-1} for $M=O_2$ at 298 K.
$k = 3.0\times10^{-18} \exp(-200/T)$ cm^3 molecule^{-1} s^{-1} for $M=O_2$ over the temperature range 100–450 K.
$k \leq 1.4\times10^{-19}$ cm^3 molecule^{-1} s^{-1} for $M=N_2$ at 298 K.
$k = 5\times10^{-18}$ cm^3 molecule^{-1} s^{-1} for $M=H_2O$ at 298 K.
$k \leq 2\times10^{-20}$ cm^3 molecule^{-1} s^{-1} for $M=CO_2$ at 298 K.

Reliability
$\Delta \log k = \pm 0.2$ for $M=O_2$ at 298 K.
$\Delta (E/R) = \pm 200$ K for $M=O_2$.
$\Delta \log k = \pm 0.3$ for $M=H_2O$ at 298 K.

Comments on Preferred Values
The preferred value of $k(M=O_2)$ is based on the results of Raja *et al.*,[1] Billington and Borrell,[2] Borrell *et al.*[3] and Leiss *et al.*[4] The temperature dependence of Billington and Borrell[2] is adopted in this evaluation. The previous CODATA recommendations[5] for $M=N_2$, H_2O and CO_2 are unchanged. The preferred values are identical to our previous evaluation, IUPAC, 1992.[6]

References

[1] N. Raja, P. K. Arora, and J. P. S. Chatha, Int. J. Chem. Kinet. **18**, 505 (1986).
[2] A. P. Billington and P. Borrell, J. Chem. Soc. Faraday Trans. 2, **82**, 963 (1986).
[3] P. Borrell, P. M. Borrell, and M. B. Pedley, Chem. Phys. Lett. **51**, 300 (1977).
[4] A. Leiss, U. Schurath, K. H. Becker, and E. H. Fink, J. Photochem. **8**, 211 (1978).
[5] CODATA, Supplement II, 1984 (see references in Introduction).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$

$\Delta H^\circ = 12.2$ kJ·mol^{-1}

Rate coefficient data

No new data have been published since our last evaluation.

Preferred Values

$k = 3.8\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.2\times10^{-11} \exp(-2840/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280–360 K.

Reliability
$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

Whereas there is good agreement on the room temperature value, the temperature coefficient appears less certain. In view of the consistency of the results from Ref. 1, which were obtained by two completely different techniques, we favor their temperature coefficient over that from Ref. 2. The preferred values of our previous evaluation are unchanged.[3]

References

[1] K. H. Becker, W. Groth, and U. Schurath, Chem. Phys. Lett. **14**, 48 (1972).
[2] F. D. Findlay and D. R. Snelling, J. Chem. Phys. **54**, 2750 (1971).
[3] CODATA, Supplement I, 1982 (see references in Introduction).

$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^3\Sigma_g^-) + M$ (1)
$\rightarrow O_2(^1\Delta_g) + M$ (2)

$\Delta H°(1) = -156.9$ kJ·mol^{-1}
$\Delta H°(2) = -62.6$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{1}	M	Temp./K	Reference	Comments
Absolute Rate Coefficients				
5.6×10^{-17}	O_2	302	Knickelbein *et al.*, 1987[1]	(a)
$<1.0\times10^{-16}$	O_2	298	Shi and Barker, 1990[2]	(b)
$(2.2\pm0.2)\times10^{-15}$	N_2	298	Wildt *et al.*, 1988[3]	(c)
$(2.32\pm0.14)\times10^{-15}$	N_2	298	Shi and Barker, 1990[2]	(b)
$(6.0\pm0.3)\times10^{-12}$	H_2O	298	Shi and Barker, 1990[2]	(b)
$(2.4\pm0.4)\times10^{-13}$	CO_2	298	Wildt *et al.*, 1988[3]	(c)
$(4.0\pm0.1)\times10^{-13}$	CO_2	298	Shi and Barker, 1990[2]	(b)
Reviews and Evaluations				
4.0×10^{-17}	O_2	298	IUPAC, 1989[4]	(d)
2.0×10^{-15}	N_2	200-350		(e)
8.0×10^{-14}	$O(^3P)$	298		(f)
4.0×10^{-12}	H_2O	298		(g)
4.1×10^{-13}	CO_2	245-360		(h)
3.9×10^{-17}	O_2	298	NASA, 1994[5]	(i)
2.1×10^{-15}	N_2	200-300		(j)
8×10^{-14}	$O(^3P)$	298		(k)
5.4×10^{-12}	H_2O	298		(l)
4.2×10^{-13}	CO_2	200-300		(m)

Comments

(a) $O_2(^1\Sigma_g^+)$ was generated by excitation of O_2 with a tunable alexandrite laser at 760 nm, and detected by measuring the fluorescence emission at 860 nm.

(b) $O_2(^1\Sigma_g^+)$ was generated by the reaction $O(^1D) + O_2 \rightarrow O + O_2(^1\Sigma_g^+)$, with $O(^1D)$ atoms being formed by photolysis of O_3/O_2 mixtures at 308 nm. Rate coefficients were measured by detecting the decay of $O_2(^1\Sigma_g^+)$ at 762 nm.

(c) $O_2(^1\Sigma_g^+)$ was formed by direct laser excitation of O_2 at 600–800 nm, and detected by fluorescence at 600–900 and 1270 nm.

(d) Based on the data of Thomas and Thrush,[6] Martin *et al.*,[7] Lawton *et al.*,[8] and Chatha *et al.*[9]

(e) Based on the data of Kohse-Höinghaus and Stuhl,[10] Martin *et al.*,[7] Chatha *et al.*,[9] and Choo and Leu.[11]

(f) Value of Slanger and Black.[12]

(g) Value of Thomas and Thrush.[6]

(h) Based on the results of Choo and Leu,[11] Filseth *et al.*,[13] Noxon,[14] Davidson *et al.*,[15] Avilés *et al.*,[16] Muller and Houston,[17] Borrell *et al.*,[18] and Boodaghians *et al.*[19]

(i) Based on the data of Martin *et al.*,[7] Lawton *et al.*,[8] and Lawton and Phelps.[20]

(j) Based on the data of Izod and Wayne,[21] Stuhl and Welge,[22] Filseth *et al.*,[13] Martin *et al.*,[7] Kohse-Höinghaus and Stuhl,[10] Choo and Leu,[11] Wildt *et al.*,[3] and Shi and Barker.[2]

(k) Based on the data of Slanger and Black.[12]

(l) Based on the data of Stuhl and Niki,[23] Filseth *et al.*,[13] Wildt *et al.*,[3] and Shi and Barker.[2]

(m) Based on the data of Filseth *et al.*,[13] Davidson *et al.*,[15] Avilés *et al.*,[16] Muller and Houston,[17] Choo and Leu,[11] Wildt *et al.*,[3] and Shi and Barker.[2]

Preferred Values

$k=4.0\times10^{-17}$ cm^3 molecule^{-1} s^{-1} for $M=O_2$ at 298 K.

$k=2.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} for $M=N_2$ over the temperature range 200–350 K.

$k=8.0\times10^{-14}$ cm^3 molecule^{-1} s^{-1} for M=O(^{3}P) at 298 K.

$k=4.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} for M=H_2O at 298 K.

$k=4.1\times10^{-13}$ cm^3 molecule^{-1} s^{-1} for M=CO_2 over the temperature range 245–360 K.

Reliability

Δlog $k=\pm0.3$ for M=O_2, O(^{3}P), H_2O at 298 K.

Δlog $k=\pm0.10$ for M=N_2, CO_2 at 298 K.

$\Delta(E/R)=\pm200$ K for M=N_2, CO_2.

Comments on Preferred Values

The results of the recent studies of Knickelbein *et al.*,[1] Shi and Barker,[2] and Wildt *et al.*[3] are in generally good agreement with those of our earlier evaluation.[4] Thus, no changes are recommended. However, it has to be noted that Wildt *et al.*[3] and Knickelbein *et al.*[1] report yields of $O_2(^1\Delta_g)$ formation, k_2/k, which are greater than 0.9 and close to unity, respectively.

References

[1] M. B. Knickelbein, K. L. Marsh, O. E. Ulrich, and G. E. Busch, J. Chem. Phys. 87, 2392 (1987).

[2] J. Shi and J. R. Barker, Int. J. Chem. Kinet. 22, 1283 (1990).

[3] J. Wildt, G. Bednarek, E. H. Fink, and R. P. Wayne, Chem. Phys. **122**, 463 (1988).

[4] IUPAC, Supplement III, 1989 (see references in Introduction).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

[6] R. G. O. Thomas and B. A. Thrush, J. Chem. Soc. Faraday Trans. 2, **71**, 664 (1975).

[7] L. R. Martin, R. B. Cohen, and J. F. Schatz, Chem. Phys. Lett. **41**, 394 (1976).

[8] S. A. Lawton, S. E. Novick, H. P. Broida, and A. V. Phelps, J. Chem. Phys. **66**, 1381 (1977).

[9] J. P. S. Chatha, P. K. Arora, S. M. T. Nalini Raja, P. B. Kulkarni, and K. G. Vohra, Int. J. Chem. Kinet. **11**, 175 (1979).

[10] K. Kohse-Höinghaus and F. Stuhl, J. Chem. Phys. **72**, 3720 (1980).

[11] K. Y. Choo and M.-T. Leu, Int. J. Chem. Kinet. **17**, 1155 (1985).

[12] T. G. Slanger and G. Black, J. Chem. Phys. **70**, 3434 (1979).

[13] S. V. Filseth, A. Zia, and K. H. Welge, J. Chem. Phys. **52**, 5502 (1970).

[14] J. F. Noxon, J. Chem. Phys. **52**, 1852 (1970).

[15] J. A. Davidson, K. E. Kear, and E. W. Abrahamson, J. Photochem. **1**, 307 (1972/73).

[16] R. G. Avilés, D. F. Muller, and P. L. Houston, Appl. Phys. Lett. **37**, 358 (1980).

[17] D. F. Muller and P. L. Houston, J. Phys. Chem. **85**, 3563 (1981).

[18] P. M. Borrell, P. Borrell, and K. R. Grant, J. Chem. Phys. **78**, 748 (1983).

[19] R. B. Boodaghians, P. M. Borrell, and P. Borrell, Chem. Phys. Lett. **97**, 193 (1983).

[20] S. A. Lawton and A. V. Phelps, J. Chem. Phys. **69**, 1055 (1978).

[21] T. P. J. Izod and R. P. Wayne, Proc. R. Soc. London, Ser. A **308**, 81 (1968).

[22] F. Stuhl and K. H. Welge, Can. J. Chem. **47**, 1870 (1969).

[23] F. Stuhl and H. Niki, Chem. Phys. Lett. **7**, 473 (1970).

$$
\begin{aligned}
O_2(^1\Sigma_g^+) + O_3 &\rightarrow 2O_2 + O &(1)\\
&\rightarrow O_2(^1\Delta_g) + O_3 &(2)\\
&\rightarrow O_2(^3\Sigma_g^-) + O_3 &(3)
\end{aligned}
$$

$\Delta H^\circ(1) = -50.4$ kJ·mol^{-1}

$\Delta H^\circ(2) = -62.6$ kJ·mol^{-1}

$\Delta H^\circ(3) = -156.9$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2+k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.96\pm0.09)\times10^{-11}$	300	Shi and Barker, 1990[1]	(a)
$(2.06\pm0.22)\times10^{-11}$	300	Turnipseed *et al.*, 1991[2]	(b)
Reviews and Evaluations			
2.2×10^{-11}	295–360	IUPAC, 1989[3]	(c)
$k_1=1.5\times10^{-11}$	298		
2.2×10^{-11}	200–300	NASA, 1994[4]	(d)

Comments

(a) $O_2(^1\Sigma_g^+)$ was generated by the reaction $O(^1D) + O_2 \rightarrow O + O_2(^1\Sigma_g^+)$, with O(^{1}D) being formed by photolysis of O_3/O_2 mixtures at 308 nm. Rate coefficients were measured by detecting the decay of $O_2(^1\Sigma_g^+)$ at 762 nm.

(b) Laser flash photolysis study of O_3 at 193 and 222 nm. Measurements of quantum yields for the formation of O(^{1}D) and O(^{3}P) were by time-resolved resonance fluorescence. Rate coefficients for the global reaction of $O_2(^1\Sigma_g^+)$ with O_3 were derived by modeling.

(c) Based on the rate coefficients reported in Refs. 5–10.

(d) Based on the data of Refs. 1, 2, and 5–10.

Preferred Values

$k = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 295–360 K.
$k_1 = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta \log k_1 = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The two more recent studies[1,2] are in very good agreement with the previous evaluations[3,11,12] at room temperature. The preferred values from our earlier evaluations remain unchanged.[3,11,12] Channel 1 accounts for 70±20% of the total reaction.[7,8]

References

[1] J. Shi and J. R. Barker, Int. J. Chem. Kinet. **22**, 1283 (1990).
[2] A. A. Turnipseed, G. L. Vaghjiani, T. Gierczak, J. E. Thompson, and A. R. Ravishankara, J. Chem. Phys. **95**, 3244 (1991).
[3] IUPAC, Supplement III, *1989* (see references in Introduction).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] R. Gilpin, H. I. Schiff, and K. H. Welge, J. Chem. Phys. **55**, 1087 (1971).
[6] D. R. Snelling, Can. J. Chem. **52**, 257 (1974).
[7] T. G. Slanger and G. Black, J. Chem. Phys. **70**, 3434 (1979).
[8] S. T. Amimoto and R. Wiesenfeld, J. Chem. Phys. **72**, 3899 (1980).
[9] P. J. Ogren, T. J. Sworski, C. J. Hochanadel, and J. M. Cassell, J. Phys. Chem. **86**, 238 (1982).
[10] K. Y. Choo and M.-T. Leu, Int. J. Chem. Kinet. **17**, 1155 (1985).
[11] CODATA, Supplement I, 1982 (see references in Introduction).
[12] CODATA, Supplement II, 1984 (see references in Introduction).

$O_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$O_2 + h\nu \rightarrow O(^3P) + O(^3P)$	494	242
$\rightarrow O(^3P) + O(^1D)$	683	175
$\rightarrow O(^1D) + O(^1D)$	873	137
$\rightarrow O(^3P) + O(^1S)$	898	132

Absorption cross-section data

Wavelength range/nm	Reference	Comment
180–195	Yoshino *et al.*, 1992 [1]	(a)

Comments

(a) Absorption cross-sections of the Schumann-Runge bands (1,0)-(12,0) in the window region between the rotational lines were measured over the pressure range 1.8–1000 mbar O_2, allowing the pressure-dependent absorption to be separated from the main cross-sections. The resulting Herzberg continuum sections below 200 nm are significantly smaller than any previous measurements.

Preferred Values

Absorption cross-section of O_2 in the 205–240 nm region of the Herzberg continuum

λ/nm	$10^{24}\sigma$/cm^2	λ/nm	$10^{24}\sigma$/cm^2
205	7.35	223	3.89
207	7.05	225	3.45
209	6.68	227	2.98
211	6.24	229	2.63
213	5.89	231	2.25
215	5.59	233	1.94
217	5.13	235	1.63
219	4.64	237	1.34
221	4.26	239	1.10
		240	1.01

Comments on Preferred Values

The recommended absorption cross-section values for the Herzberg continuum are taken from the study of Yoshino *et al.*,[2] where values are tabulated for every nm from 205–240 nm. These values were derived from an analysis and combination of the data of Cheung *et al.*[3] and Jenouvrier *et al.*[4] They are in agreement with the results of Johnston *et al.*[5] They are consistent with the lower absorption cross-section values inferred from balloon-borne measurements of solar irradiance attenuation in the stratosphere by Frederick and Mentall,[6] Herman and Mentall,[7] and Anderson and Hall.[8] Herzberg continuum cross-section values under the S-R bands (<200 nm) have recently been determined more accurately by Yoshino *et al.*[1] and are significantly smaller than any previous values.

In the Schumann-Runge wavelength region (175–200 nm), a detailed analysis of the penetration of solar radiation requires absorption cross-section measurements with very high spectral resolution. Absorption cross-section values for the (0, 0)-(12, 0) S-R bands measured by the Harvard-Smithsonian group[1,9–17] are the first set of values which are independent of instrumental width. Band oscillator strengths for these bands have been determined by direct numerical integration of these absolute cross-section values. Minschwaner *et al.*[18,19] have fitted O_2 cross-sections for the frequency range 49000–57000 cm^{-1} (175–204 nm) with temperature dependent polynomial expressions for 130–500 K using the latest laboratory spectroscopic data. This model provides an efficient and accurate means of determining S-R band absorption cross-sections at 0.5 cm^{-1} resolution. These high resolution calculated values differ from the WMO[20] recommendations by up to 10–20% at some wavelengths. Mean-band parameterizations of O_2 absorption in the S-R bands for calculating UV transmission and photolysis rates have been presented by Murtagh[21] and by Nicolet and Kennes.[22]

The effect on ozone formation in the 214 nm photolysis of oxygen due to O_2-O_2 collision pairs at high O_2 pressure and the effect of high N_2 pressure have been studied by Horowitz *et al.*[23] Greenblatt *et al.*[24] studied the absorption spectrum of O_2 and O_2-O_2 collision pairs over the wavelength range 330–1140 nm for O_2 pressures from 1 to 55 bar at 298 K. Band centers, band widths, and absorption cross-sections were reported for the absorption features in this wavelength region.

References

[1] K. Yoshino, J. R. Esmond, A. S. C. Cheung, D. E. Freeman, and W. H. Parkinson, Planet. Space Sci. **40**, 185 (1992).

[2] K. Yoshino, A. S. C. Cheung, J. R. Esmond, W. H. Parkinson, D. E. Freeman, S. L. Guberman, A. Jenouvrier, B. Coquart, and M. F. Merienne, Planet. Space Sci. **36**, 1469 (1988).

[3] A. S. C. Cheung, K. Yoshino, W. H. Parkinson, S. L. Guberman, and D. E. Freeman, Planet. Space Sci. **34**, 1007 (1986).

[4] A. Jenouvrier, B. Coquart, and M. F. Merienne, J. Quant. Spectrosc. Radiat. Transfer **36**, 349 (1986).

[5] H. S. Johnston, M. Paige, and F. Yao, J. Geophys. Res. **89**, 11661 (1984).

[6] J. E. Frederick and J. E. Mentall, Geophys. Res. Lett. **9**, 461 (1982).

[7] J. R. Herman and J. E. Mentall, J. Geophys. Res. **87**, 8967 (1982).

[8] G. P. Anderson and L. A. Hall, J. Geophys. Res. **88**, 6801 (1983); *ibid.* **91**, 14509 (1986).

[9] K. Yoshino, D. E. Freeman, J. R. Esmond, and W. H. Parkinson, Planet. Space Sci. **31**, 339 (1983).

[10] K. Yoshino, D. E. Freeman, and W. H. Parkinson, J. Phys. Chem. Ref. Data **13**, 207 (1984).

[11] A. S. C. Cheung, K. Yoshino, W. H. Parkinson, and D. E. Freeman, Can. J. Phys. **62**, 1752 (1984).

[12] K. Yoshino, D. E. Freeman, J. R. Esmond, and W. H. Parkinson, Planet. Space Sci. **35**, 1067 (1987).

[13] K. Yoshino, D. E. Freeman, J. R. Esmond, R. S. Friedman, and W. H. Parkinson, Planet. Space Sci. **36**, 1201 (1988); *ibid.* **37**, 419 (1989).

[14] A. S. C. Cheung, K. Yoshino, D. E. Freeman, R. S. Friedman, A. Dalgarno, and W. H. Parkinson, J. Mol. Spectrosc. **134**, 362 (1989).

[15] A. S. C. Cheung, K. Yoshino, J. R. Esmond, S. S. L. Chiu, D. E. Freeman, and W. H. Parkinson, J. Chem. Phys. **92**, 842 (1990).

[16] S. S. L. Chiu, A. S. C. Cheung, K. Yoshino, J. R. Esmond, D. E. Freeman, and W. H. Parkinson, J. Chem. Phys. **93**, 5539 (1990).

[17] K. Yoshino, J. R. Esmond, A. S. C. Cheung, D. E. Freeman, and W. H. Parkinson, J. Geophys. Res. **95**, 11743 (1990).

[18] K. Minschwaner, G. P. Anderson, L. A. Hall, and K. Yoshino, J. Geophys. Res. **97**, 10103 (1992).

[19] K. Minschwaner, R. J. Salawitch, and M. B. McElroy, J. Geophys. Res. **98**, 10543 (1993).

[20] WMO Global Ozone Research and Monitoring Project Report No. 16, Atmospheric Ozone 1985, Chapter 7 (1986).

[21] D. P. Murtagh, Planet. Space Sci. **36**, 819 (1988).

[22] M. Nicolet and R. Kennes, Planet. Space Sci. **37**, 459 (1989).

[23] A. Horowitz, W. Schneider, and G. K. Moortgat, J. Phys. Chem. **93**, 7859 (1989); *ibid.* **94**, 2904 (1990).

[24] G. D. Greenblatt, J. J. Orlando, J. B. Burkholder, and A. R. Ravishankara, J. Geophys. Res. **95**, 18577 (1990).

$O_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Sigma_g)$	(1)	101	1180
$\rightarrow O(^3P) + O_2(^1\Delta_g)$	(2)	196	611
$\rightarrow O(^3P) + O_2(^1\Sigma_g^+)$	(3)	258	463
$\rightarrow O(^1D) + O_2(^3\Sigma_g)$	(4)	291	411
$\rightarrow O(^1D) + O_2(^1\Delta_g)$	(5)	386	310
$\rightarrow O(^1D) + O_2(^1\Sigma_g^+)$	(6)	448	267

Absorption cross-section data

Wavelength range/nm	Reference	Comment
195–345	Daumont *et al.*, 1992[1]	(a)
195–345	Brion *et al.*, 1993[2]	(b)
185–254	Yoshino *et al.*, 1993[3]	(c)
410–760	Burkholder and Talukdar, 1994[4]	(d)

Quantum yield data

Measurement	λ/nm	Reference	Comment
ϕ [O(^{1}D)]	222	Turnipseed *et al.*, 1991[5]	(e)
ϕ [O(^{1}D)]	221–243.5	Cooper, Neill and Wiesenfeld, 1993[6]	(f)
ϕ [O_2($^1\Delta$)]	270–329	Ball *et al.*, 1993[7]	(g)
ϕ [O(^{1}D)]	305-325	Michelsen *et al.*, 1991[8]	(h)

Comments

(a) Measured at 295 K with a spectral resolution of 0.005 nm. Two independent methods were used to measure the ozone pressure.

(b) Extension of study reported in Daumont *et al.*[1] to low temperatures, 220–295 K.

(c) Measured at 195, 228, and 295 K. Relative cross-sections measured over the range 185–254 nm were normalized using absolute values measured at 12 fixed wavelengths in this region.

(d) Relative values measured at 220–298 K were normalized using absolute values reported by Anderson and Mauersberger[9] for five He-Ne laser wavelengths.

(e) Laser photolysis with time-resolved resonance fluorescence detection of O(^{3}P). At 222 nm ϕ[O(^{3}P)]=0.13 ±0.02 and ϕ[O(^{1}D)]=0.87±0.04. Results were also reported for 193 nm.

(f) Tunable dye laser photolysis with detection of O(^{1}D) by the weak 630 nm fluorescence from the spin-forbidden $^1D \rightarrow {}^3P$ transition. Relative O(^{1}D) quantum yields were normalized to the value of 0.87±0.04 at 222 nm reported by Turnipseed *et al.*[5]

(g) Relative O_2($^1\Delta$) quantum yields in the tunable dye laser photolysis of ozone were determined by [2+1] resonance enhanced multiphoton ionization (REMPI). The quantum yield agrees with that recommended for O(^{1}D), except at the longer wavelengths where O_2($^1\Delta$) is still produced with a yield of $\geqslant$0.10.

(h) Authors developed a model accounting for absorption by vibrationally and rotationally excited ozone and, using this model to examine published measurements of the quantum yield of O(^{1}D) production in the Huggins band, concluded that ϕ [O(^{1}D)] has a value of 0.2–0.3 for wavelengths between 312 and 320 nm at 298 K.

Preferred Values

Ozone absorption cross-sections at 273 K averaged over spectral internals

Int #	Δλ/nm	$10^{20}\sigma$/cm^2	Int #	Δλ/nm	$10^{20}\sigma$/cm^2
1	175.4–177.0	81.1	31	238.1–241.0	797
2	178.6	79.9	32	243.9	900
3	180.2	78.6	33	246.9	1000
4	181.8	76.3	34	250.1	1080
5	183.5	72.9	35	253.2	1130
6	185.2	68.8	36	256.4	1150
7	186.9	62.2	37	259.7	1120
8	188.7	57.6	38	263.2	1060
9	190.5	52.6	39	266.7	965
10	192.3	47.6	40	270.3	834
11	194.2	42.8	41	274.0	692
12	196.1	38.3	42	277.8	542
13	198.0	34.7	43	281.7	402
14	200.0	32.3	44	285.7	277
15	202.0	31.4	45	289.9	179
16	204.1	32.6	46	294.1	109
17	206.2	36.4	47	298.5	62.4
18	208.3	43.4	48	303.0	34.3
19	210.5	54.2	49	307.7	18.5
20	212.8	69.9	50	312.5	9.8
21	215.0	92	51	317.5	5.0
22	217.4	119	52	322.5	2.49
23	219.8	155	53	327.5	1.20
24	222.2	199	54	332.5	0.617
25	224.7	256	55	337.5	0.274
26	227.3	323	56	342.5	0.117
27	229.9	400	57	347.5	0.059
28	232.6	483	58	352.5	0.027
29	235.3	579	59	357.5	0.011
30	238.1	686	60	362.5	0.005

σ=(1147±20)×10^{-20}cm^2 at 253.7 nm

Ozone absorption cross-sections in the visible spectral region

λ/nm	$10^{23}\sigma/\mathrm{cm}^2$	λ/nm	$10^{23}\sigma/\mathrm{cm}^2$
410	1.2	560	394
420	2.2	580	459
440	11.2	600	511
460	32.8	620	400
480	68.4	640	296
500	122	660	209
520	182	680	136
540	291	700	91

Quantum yields for O(^{1}D) production, ϕ_5, from O_3 photolysis at 298 K

λ/nm	Quantum yield
290	$\phi_5=0.95$
295	0.95
300	0.95
305	0.95
306	0.93
307	0.89
308	0.81
309	0.68
310	0.53
311	0.38
312	0.25
313	0.14
314	0.08
315	0.05
316	0.03
317	0.02
318	0.01
319	0.00
320	0.00

Comments on Preferred Values

Absorption cross-sections. The recommended absorption cross-section values at 273 K for the wavelength range 175–362 nm are averaged values for the standard spectral intervals used in modeling calculations. These values have been adopted from the NASA 1994 review,[10] which accepted the values tabulated in the WMO 1986 review,[11] except for the region 185–225 nm where the values were taken from the study of Molina and Molina.[12] The value recommended for the mercury line at 253.7 nm is based on results reported by Hearn,[13] Molina and Molina[12] and Mauersberger *et al.*[14] The values for the wavelength range 400–700 nm are taken from Burkholder and Talukdar.[4] The spectroscopy of ozone has been reviewed by Steinfeld, Adler-Golden and Gallagher.[15]

Quantum yields

The quantum yield values for 305–320 nm and 298 K have been calculated from the expression for $\phi_5(\lambda,T)$ given in the NASA 1994 review.[10] That expression is based on the high resolution laser data of Arnold *et al.*,[16] Brock and Watson[17] and Trolier and Wiesenfeld.[18] The temperature dependence is based on the xenon arc lamp-monochromator results reported in Moortgat and Kudszus.[19] An extensive discussion of quantum yield data for this region and extending down to 220 nm is given in the NASA 1994 review,[10] to which the reader is referred. There it is noted that for the wavelength region 220–280 nm the more recent studies yield ϕ_5 values around 0.85–0.90, and that for the region 290–305 nm the value $\phi_5=0.95$ is recommended.[10]

References

[1] D. D. Daumont, J. Brion, J. Charbonnier, and J. Malicet, J. Atmos. Chem. **15**, 145 (1992).

[2] J. Brion, A. Chakir, D. Daumont, J. Malicet, and C. Parisse, Chem. Phys. Lett. **213**, 1010 (1993).

[3] K. Yoshino, J. R. Esmond, D. E. Freeman, and W. H. Parkinson, J. Geophys. Res. **98**, 5205 (1993).

[4] J. B. Burkholder and R. K. Talukdar, Geophys. Res. Lett. **21**, 581 (1994).

[5] A. A. Turnipseed, G. L. Vaghjiani, T. Gierczak, J. E. Thompson, and A. R. Ravishankara, J. Chem. Phys. **95**, 3244 (1991).

[6] I. A. Cooper, P. J. Neill, and J. R. Wiesenfeld, J. Geophys. Res. **98**, 12795 (1993).

[7] S. M. Ball, G. Hancock, I. J. Murphy, and S. P. Rayner, Geophys. Res. Lett. **20**, 2063 (1993).

[8] H. A. Michelsen, R. J. Salawitch, P. O. Wennberg, and J. G. Anderson, Geophys. Res. Lett. **21**, 2227 (1994).

[9] S. M. Anderson and K. Mauersberger, Geophys. Res. Lett. **19**, 933 (1992).

[10] NASA Evaluation No. 11, 1994 (see references in Introduction).

[11] WMO Global Ozone Research and Monitoring Project Report No. 16, Atmospheric Ozone 1985, Chapter 7 (1986).

[12] L. T. Molina and M. J. Molina, J. Geophys. Res. **91**, 14501 (1986).

[13] A. G. Hearn, Proc. Phys. Soc. London, **78**, 932 (1961).

[14] K. Mauersberger, J. Barnes, D. Hanson, and J. Morton, Geophys. Res. Lett. **13**, 671 (1986); K. Mauersberger, D. Hanson, J. Barnes, and J. Morton, J. Geophys. Res. **92**, 8480 (1987).

[15] J. I. Steinfeld, S. M. Adler-Golden, and J. W. Gallagher, J. Phys. Chem. Ref. Data **16**, 911 (1987).

[16] I. Arnold, F. J. Comes, and G .K. Moortgat, Chem. Phys. **24**, 211 (1977).

[17] J. C. Brock and R. T. Watson, Chem. Phys. **46**, 477 (1980).

[18] M. Trolier and J. R. Wiesenfeld, J. Geophys. Res. **93**, 7119 (1988).

[19] G. K. Moortgat and E. Kudszus, Geophys. Res. Lett. **5**, 191 (1978).

4.2. Hydrogen Species

$$\begin{aligned} H + HO_2 &\rightarrow H_2 + O_2 \quad (1)\\ &\rightarrow 2HO \quad (2)\\ &\rightarrow H_2O+O \quad (3) \end{aligned}$$

$\Delta H^\circ(1) = -232.6\ \text{kJ}\cdot\text{mol}^{-1}$
$\Delta H^\circ(2) = -154.0\ \text{kJ}\cdot\text{mol}^{-1}$
$\Delta H^\circ(3) = -225.2\ \text{kJ}\cdot\text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2 + k_3$)

$k = 8.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245–300 K.
$k_1 = 5.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245–300 K.
$k_2 = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245–300 K.
$k_3 = 2.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245–300 K.

Reliability

$\Delta \log k = \pm 0.1$ over the temperature range 245–300 K.
$\Delta(E/R) = \pm 200$ K.
$\Delta \log k_1 = \pm 0.5$ over the temperature range 245–300 K.
$\Delta \log k_2 = \pm 0.1$ over the temperature range 245–300 K.
$\Delta \log k_3 = \pm 0.5$ over the temperature range 245–300 K.

Comments on Preferred Values

The study of Keyser[1] is the most detailed to date. Several species were monitored and the possible effects of side reactions were carefully analyzed. Values obtained for the overall rate coefficient and the branching ratios agree with the values obtained by Sridharan *et al.*[2] who used a similar technique. The recommended values for k and the branching ratios are the means of the values from these two studies. In both cases k_1/k was not measured directly but obtained by difference. A direct measurement of this branching ratio is desirable.

The yield of $O_2(^1\Sigma_g^+)$ has been measured by Hislop and Wayne,[3] Keyser *et al.*,[4] and Michelangeli *et al.*[5] who report values of $(2.8 \pm 1.3) \times 10^{-4}$, $<8 \times 10^{-3}$ and $<2.1 \times 10^{-2}$, respectively. Keyser[1] observed no effect of temperature on the rate coefficient k over the small range studied. This suggests that the value of $k_2 = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 349 K obtained by Pagsberg *et al.*[6] is too low or there is a substantial negative temperature coefficient. We provisionally recommend $E/R = 0$ but only over the temperature range 245–300 K. The preferred values are identical to our previous evaluation, IUPAC, 1992.[7]

References

[1] L. F. Keyser, J. Phys. Chem. **90**, 2994 (1986).
[2] U. C. Sridharan, L. X. Qiu, and F. Kaufman, J. Phys. Chem. **86**, 4569 (1982).
[3] J. R. Hislop and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **73**, 506 (1977).
[4] L. F. Keyser, K. Y. Choo, and M. T. Leu, Int. J. Chem. Kinet. **17**, 1169 (1985).
[5] D. V. Michelangeli, K. Y. Choo, and M. T. Leu, Int. J. Chem. Kinet. **20**, 915 (1988).
[6] P. B. Pagsberg, J. Eriksen, and H. C. Christensen, J. Phys. Chem. **83**, 582 (1979).
[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$H + O_2 + M \rightarrow HO_2 + M$

$\Delta H^\circ = -203.4\ \text{kJ}\cdot\text{mol}^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.2) \times 10^{-32}$ [Ar]	298	Carleton, Kessler, and Marinelli, 1993[1]	(a)
$2.9 \times 10^{-33} \exp[(825 \pm 130)/T][N_2]$	298–580		
$3.9 \times 10^{-32} \exp[(600 \pm 1050)/T][H_2O]$	575–750		
Reviews and Evaluations			
$6.2 \times 10^{-32} (T/300)^{-1.6} [N_2]$	200–600	IUPAC, 1992[2]	(b)
$5.7 \times 10^{-32} (T/300)^{-1.6}$ [air]	200–300	NASA, 1994[3]	(c)

Comments

(a) Flash photolysis study. H atoms were generated by the 193 nm photolysis of H_2O and H_2S in excess O_2, and probed by LIF ($M=H_2O$) or Lyman-α resonance absorption at 121.6 nm ($M=Ar$, N_2). Typical pressures were varied between 50–500 Torr.

(b) Based on the study by Hsu *et al.*,[4] which is in excellent agreement with previous data from Refs. 5–8.

(c) The recommended value was an average of the measurements from Refs. 4–6.

Preferred Values

$k_0=5.4\times10^{-32}\ (T/300)^{-1.8}\ [N_2]\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 200–600 K.

Reliability

$\Delta\log k_0=\pm0.2$ at 298 K.

$\Delta n=\pm0.6$.

Comments on Preferred Values

We have slightly modified our previous preferred values to account for the recent measurements from Carleton *et al.*[1] These new data and previous measurements from Refs. 4–8 are in good agreement.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty=7.5\times10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta\log k_\infty=\pm0.3$ at 298 K.

$\Delta n=\pm0.6$.

Comments on Preferred Values

Measurements in $M=Ar$, N_2, and CH_4 all extrapolate to the same limiting high pressure value. The results are from a single study.[7] The preferred values of k_∞ are identical to our previous evaluation, IUPAC, 1992.[2]

Intermediate Falloff Range

The measured broadening factor $F_c=0.55\pm0.15$ at 298 K for $M=N_2$ from Ref. 7 is in agreement with a calculated value of $F_c=0.66$. Representation of the measured F_c by $F_c=\exp(-T/T^*)$ gives $T^*=498$ K.

References

[1] K. L. Carleton, W. J. Kessler, and W. J. Marinelli, J. Phys. Chem. **97**, 6412 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] K.-J. Hsu, S. M. Anderson, J. L. Durant, and F. Kaufman, J. Phys. Chem. **93**, 1018 (1989).

[5] M. J. Kurylo, J. Phys. Chem. **76**, 3518 (1972).

[6] W. Wong and D. D. Davis, Int. J. Chem. Kinet. **6**, 401 (1974).

[7] C. J. Cobos, H. Hippler, and J. Troe, J. Phys. Chem. **89**, 342 (1985).

[8] A. N. Pirraglia, J. V. Michael, J. W. Sutherland, and R. B. Klemm, J. Phys. Chem. **93**, 282 (1989).

$O + HO \rightarrow O_2 + H$

$\Delta H^\circ=-70.5\ kJ\cdot mol^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k=3.3\times10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k=2.3\times10^{-11}\exp(110/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 220–500 K.

Reliability

$\Delta\log k=\pm0.1$ at 298 K.

$\Delta(E/R)=\pm100$ K.

Comments on Preferred Values

The recommended temperature dependence is based on a least-squares fit of the data of Lewis and Watson[1] and Howard and Smith,[2] which are in close agreement. Other studies at ambient temperatures[3–5] are also in excellent agreement with these results.[1,2] The reaction has been the subject of a number of theoretical studies; see Troe[6] and Miller.[7] The preferred values are identical to our previous evaluation, IUPAC, 1992.[8]

References

[1] R. S. Lewis and R. T. Watson, J. Phys. Chem. **84**, 3495 (1980).

[2] M. J. Howard and I. W. M. Smith, J. Chem. Soc. Faraday Trans. 2, **77**, 997 (1981).

[3] Wm. H. Brune, J. J. Schwab, and J. G. Anderson, J. Phys. Chem. **87**, 4503 (1983).

[4] L. F. Keyser, J. Phys. Chem. **87**, 837 (1983).

[5] M. J. Howard and I. W. M. Smith, Chem. Phys. Lett. **69**, 40 (1980).

[6] J. Troe, *22nd International Symposium on Combustion, 1988* (The Combustion Institute, Pittsburgh, PA, 1989), pp. 843–862.

[7] J. A. Miller, J. Chem. Phys. **84**, 6170 (1986).

[8] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O + HO_2 \rightarrow HO + O_2$

$\Delta H° = -224.5$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 5.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.7 \times 10^{-11} \exp(224/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The recommended value at 298 K is the mean of values obtained in the studies of Nicovich and Wine,[1] Keyser,[2] Sridharan *et al.*,[3] Ravishankara *et al.*,[4] and Brune *et al.*,[5] all of which are in excellent agreement. The temperature coefficient is the mean of the values obtained by Nicovich and Wine[1] and Keyser,[2] with the pre-exponential factor being based on this value of E/R and the recommended value of k at 298 K. The preferred values are identical to our previous evaluation, IUPAC, 1992.[6]

In the two most recent studies of the reaction mechanism, Keyser *et al.*[7] have shown that the yield of $O_2(^1\Sigma_g^+)$ from the reaction is $<1 \times 10^{-2}$ per HO_2 radical removed and Sridharan *et al.*[8] have shown, in an ^{18}O labeling experiment, that the reaction proceeds via formation of an $HO_2-^{18}O$ intermediate which dissociates to HO and ^{18}OO by rupture of an O–O bond rather than via a four center intermediate yielding $H^{18}O$ + OO.

References

[1] J. M. Nicovich and P. H. Wine, J. Phys. Chem. **91**, 5118 (1987).

[2] L. F. Keyser, J. Phys. Chem. **86**, 3439 (1982).

[3] U. C. Sridharan, L. X. Qiu, and F. Kaufman, J. Phys. Chem. **86**, 459 (1982).

[4] A. R. Ravishankara, P. H. Wine, and J. M. Nicovich, J. Chem. Phys. **78**, 6629 (1983).

[5] W. H. Brune, J. J. Schwab, and J. G. Anderson, J. Phys. Chem. **87**, 4503 (1983).

[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

[7] L. F. Keyser, K. Y. Choo, and M. T. Leu, Int. J. Chem. Kinet. **17**, 1169 (1985).

[8] U. C. Sridharan, F. S. Klein, and F. Kaufman, J. Chem. Phys. **82**, 592 (1985).

$O + H_2O_2 \rightarrow HO + HO_2$

$\Delta H° = -59.0$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.4 \times 10^{-12} \exp(-2000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–390 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values

The preferred values are based on the results of Wine *et al.*[1] and Davis *et al.*,[2] and are identical to our previous evaluation, IUPAC, 1992.[3] These two studies are in agreement with regard to the temperature dependence of the rate coefficient but the absolute values of k differ by a factor of 2 throughout the range. In both cases the preexponential factor obtained is low compared with other atom-molecule reactions. To obtain the preferred values the temperature coefficient is accepted and the pre-exponential factor adjusted to obtain agreement with the recommended value of k at 298 K, which is the mean of the values found in the two studies.

Roscoe[4] has discussed earlier work on this reaction, which was invalidated by secondary reactions affecting the measurements.

References

[1]P. H. Wine, J. M. Nicovich, R. J. Thompson, and A. R. Ravishankara, J. Phys. Chem. 87, 3948 (1983).
[2]D. D. Davis, W. Wong, and R. Schiff, J. Phys. Chem. 78, 463 (1974).
[3]IUPAC, Supplement IV, 1992 (see references in Introduction).
[4]J. M. Roscoe, Int. J. Chem. Kinet. 14, 471 (1982).

$O(^1D) + H_2 \rightarrow HO + H$ (1)
$\rightarrow O(^3P) + H_2$ (2)

$\Delta H^\circ(1) = -181.6$ kJ·mol^{-1}
$\Delta H^\circ(2) = -189.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–350 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred values are the mean of the values of Wine and Ravishankara,[1] Davidson *et al.*,[2] and Force and Wiesenfeld,[3] all of which are in excellent agreement, and are identical to our previous evaluation, IUPAC, 1992.[4] Channel (1) appears to be the predominant pathway (>95%)[5] for the reaction.

References

[1]P. H. Wine and A. R. Ravishankara, Chem. Phys. Lett. 77, 103 (1981).
[2]J. A. Davidson, H. I. Schiff, G. E. Streit, J. R. McAfee, A. L. Schmeltekopf, and C. J. Howard, J. Chem. Phys. 67, 5021 (1977).
[3]A. P. Force and J. R. Wiesenfeld, J. Chem. Phys. 74, 1718 (1981).
[4]IUPAC, Supplement IV, 1992 (see references in Introduction).
[5]P. H. Wine and A. R. Ravishankara, Chem. Phys. 69, 365 (1982).

$O(^1D) + H_2O \rightarrow 2HO$ (1)
$\rightarrow H_2 + O_2$ (2)
$\rightarrow O(^3P) + H_2O$ (3)

$\Delta H^\circ(1) = -118.5$ kJ·mol^{-1}
$\Delta H^\circ(2) = -197.1$ kJ·mol^{-1}
$\Delta H^\circ(3) = -189.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2 + k_3$)

$k = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–350 K.
$k_1 = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 < 2.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_3 < 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.
$\Delta \log k_1 = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value for k is a mean of the values of Gericke and Comes,[1] Amimoto *et al.*,[2] Lee and Slanger,[3] Wine and Ravishankara[4] and Streit *et al.*,[5] all of which are in good agreement. Our recommendations for k_2/k and k_3/k are based on the data of Zellner *et al.*[6] and Glinski and Birks[7] (k_2/k) and Zellner *et al.*[6] and Wine and Ravishankara[8] (k_3/k). The preferred values are identical to our previous evaluation, IUPAC, 1992.[9]

References

[1]K.-H. Gericke and F. J. Comes, Chem. Phys. Lett. 81, 218 (1981).
[2]S. T. Amimoto, A. P. Force, R. G. Gulotty, Jr., and J. R. Wiesenfeld, J. Chem. Phys. 71, 3640 (1979).
[3]L. C. Lee and T. G. Slanger, Geophys. Res. Lett. 6, 165 (1979).
[4]P. H. Wine and A. R. Ravishankara, Chem. Phys. Lett. 77, 103 (1981).
[5]G. E. Streit, C. J. Howard, A. L. Schmeltekopf, J. A. Davidson, and H. I. Schiff, J. Chem. Phys. 65, 4761 (1976).
[6]R. Zellner, G. Wagner, and B. Himme, J. Phys. Chem. 84, 3196 (1980).
[7]R. J. Glinski and J. W. Birks, J. Phys. Chem. 89, 3449 (1985).
[8]P. H. Wine and A. R. Ravishankara, Chem. Phys. 69, 365 (1982).
[9]IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + H_2 \rightarrow H_2O + H$

$\Delta H^\circ = -63.1$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 6.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.7 \times 10^{-12} \exp(-2100/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–450 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

There are several studies in good agreement on both the temperature coefficient and absolute values of the rate coefficient. The preferred value of k at 298 K is the mean of the results of Greiner,[1] Stuhl and Niki,[2] Westenberg and deHaas,[3] Smith and Zellner,[4] Overend *et al.*,[5] Atkinson *et al.*,[6] Tully and Ravishankara,[7] Zellner and Steinert,[8] and Ravishankara *et al.*[9] The preferred value of E/R is the mean of the values of Smith and Zellner,[4] Atkinson *et al.*,[6] and Ravishankara *et al.*[9] The preexponential factor in the rate expression is calculated to fit the preferred value of k at 298 K and that of E/R. The preferred values are identical to our previous evaluation, IUPAC, 1992.[10]

References

[1] N. R. Greiner, J. Chem. Phys. **51**, 5049 (1969).
[2] F. Stuhl and H. Niki, J. Chem. Phys. **57**, 3671 (1972).
[3] A. A. Westenberg and N. deHaas, J. Chem. Phys. **58**, 4061 (1973).
[4] I. W. M. Smith and R. Zellner, J. Chem. Soc. Faraday Trans. 2, **70**, 1045 (1974).
[5] R. Overend, G. Paraskevopoulos, and R. J. Cvetanovic, Can. J. Chem. **53**, 3374 (1975).
[6] R. Atkinson, D. A. Hansen, and J. N. Pitts, Jr., J. Chem. Phys. **63**, 1703 (1975).
[7] F. P. Tully and A. R. Ravishankara, J. Phys. Chem. **84**, 3126 (1980).
[8] R. Zellner and W. Steinert, Chem. Phys. Lett. **81**, 568 (1981).
[9] A. R. Ravishankara, J. M. Nicovich, R. L. Thompson, and F. P. Tully, J. Phys. Chem. **85**, 2498 (1981).
[10] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + HO \rightarrow H_2O + O$

$\Delta H^\circ = -71.2$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.9 \times 10^{-14} (T/298)^{2.6} \exp(945/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–500 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

There are a number of measurements[1–10] of k at temperatures close to 298 K falling in the range $(1.4–2.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. We take the mean of the more recent studies[1–6] for our preferred value at 298 K. This value is confirmed by recent measurements[11] of the pressure dependence of the HO + HO + M reaction system which allow the reactions $HO + HO \rightarrow H_2O + O$ and $HO + HO \rightarrow H_2O_2$ to be separated. The temperature coefficient is taken from an ab initio modeling study[12] which well accommodates the experimental high temperature results.

References

[1] G. K. Farquharson and R. L. Smith, Aust. J. Chem. **33**, 1425 (1980).
[2] G. Wagner and R. Zellner, Ber. Bunsenges. Phys. Chem. **85**, 1122 (1981).
[3] A. A. Westenberg and N. deHaas, J. Chem. Phys. **58**, 4066 (1973).
[4] A. McKenzie, M. F. R. Mulcahy, and J. R. Steven, J. Chem. Phys. **59**, 3244 (1973).
[5] M. A. A. Clyne and S. Down, J. Chem. Soc. Faraday Trans. 2, **70**, 253 (1974).
[6] D. W. Trainor and C. W. von Rosenberg, Jr., J. Chem. Phys. **61**, 1010 (1974).
[7] F. P. Del Greco and F. Kaufman, Discuss. Faraday Soc. **33**, 128 (1962).
[8] G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, J. Chem. Phys. **44**, 2877 (1966).
[9] W. E. Wilson and J. T. O'Donovan, J. Chem. Phys. **47**, 5455 (1967).
[10] J. E. Breen and G. P. Glass, J. Chem. Phys. **52**, 1082 (1970).
[11] R. Forster, M. Frost, D. Fulle, H. F. Hamann, H. Hippler, A. Schlepegrell, and J. Troe, J. Chem. Phys. **103**, 2949 (1995).
[12] L. B. Harding and A. F. Wagner, *22nd International Symposium on Combustion* (Combustion Institute, Pittsburgh, 1988), p. 983.

$HO + HO + M \rightarrow H_2O_2 + M$

$\Delta H^\circ = -214.9$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
6.9×10^{-31} [N_2]	298	Fulle *et al.*, 1996[1]	(a)
Reviews and Evaluations			
$8.0\times10^{-31}(T/300)^{-0.8}$ [N_2]	200–300	IUPAC, 1992[2]	(b)
6.9×10^{-31} $(T/300)^{-0.8}$ [air]	200–300	NASA, 1994[3]	(c)

Comments

(a) Laser flash photolysis system with saturated LIF detection of HO radicals. Measurements were made between 1 and 180 bar. Falloff extrapolation was carried out with $F_c=0.5$ at 298 K. Separation between the reactions $HO + HO + M \rightarrow H_2O_2 + M$ and $HO + HO \rightarrow H_2O + O$ was made from the pressure dependence.

(b) Based on the measurements of Zellner *et al.*,[4] Trainor and von Rosenberg,[5] and preliminary results from Ref. 1. The temperature dependence was obtained from the theoretical analysis of Ref. 6.

(c) Based on direct measurements from Zellner *et al.*[4]

Preferred Values

$k_0=6.9\times10^{-31}$ $(T/300)^{-0.8}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta\log k_0=\pm0.1$ at 298 K.

$\Delta n=\pm0.5$.

Comments on Preferred Values

The previously noted[3] discrepancies between the results from Refs. 4 and 5 disappear when the pressure dependence of the reaction is analyzed over the wide range applied in Ref. 1. By this representation the reactions $HO + HO + M \rightarrow H_2O_2 + M$ and $HO + HO \rightarrow H_2O + O$ can be separated conveniently. The preferred values then are the average of results from Refs. 1, 4, and 5, based on a falloff curve using $F_c=0.5$ at 298 K. The temperature dependence of k_0 is from the theoretical analysis of Ref. 6.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.6×10^{-11}	298	Fulle *et al.*, 1996[1]	(a)
Reviews and Evaluations			
3.0×10^{-11}	200–300	IUPAC, 1992[2]	(b)
1.5×10^{-11}	200–300	NASA, 1994[3]	(c)

Comments

(a) See comment (a) for k_0.

(b) The new experiments from Ref. 1, together with the analysis[6] of photolysis and thermal dissociation rates, provide a consistent picture of the falloff curve. A value of $F_c=0.5$ is recommended over the temperature range 200–300 K.

(c) See comment (c) for k_0.

Preferred Values

$k_\infty=2.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta\log k_\infty=\pm0.2$ over the temperature range 200–300 K.

Comments on Preferred Values

The falloff curve from Ref. 1 now allows for a reliable extrapolation to k_∞ at 298 K. The temperature dependence of

k_∞ is probably small,[6] although more extensive experiments and a more detailed theoretical analysis are needed.

References

[1] D. Fulle, H. F. Hamann, H. Hippler, and J. Troe, J. Chem. Phys. **105**, 1001 (1996).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] R. Zellner, F. Ewig, R. Paschke, and G. Wagner, J. Phys. Chem. **92**, 4184 (1988).

[5] D. W. Trainor and C. W. von Rosenberg, Jr., J. Chem. Phys. **61**, 1010 (1974).

[6] L. Brouwer, C. J. Cobos, J. Troe, H. R. Düball, and F. F. Crim, J. Chem. Phys. **86**, 6171 (1987).

$HO + HO_2 \rightarrow H_2O + O_2$

$\Delta H° = -295.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=1.1\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=4.8\times10^{-11}\exp(250/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–400 K.

Reliability

$\Delta\log k=\pm0.1$ at 298 K.

$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

There has been some controversy over the effects of pressure on the rate coefficient for this reaction. Early discharge-flow measurements at low pressures (1–10 Torr) consistently gave values of k approximately a factor of 2 lower than those obtained by other techniques at pressures close to atmospheric. The discharge-flow study of Keyser[1] appears to have resolved the problem. His results[1] suggest that the presence of small quantities of H and O present in previous discharge-flow studies could have led to erroneously low values of k, and that there is no evidence for any variation in k with pressure. These findings[1] are accepted and we take the expression of Keyser[1] for k as our recommendation. There are a number of other studies in excellent agreement with the value recommended for k at 298 K, which is identical to our previous evaluation, IUPAC, 1992.[2]

In another discharge-flow study Keyser *et al.*,[3] by monitoring the $O_2(b^1\Sigma_g^+)\rightarrow X(^3\Sigma_g^-)$ transition at 762 nm, have shown that the yield of $O_2(b^1\Sigma_g^+)$ from the reaction is small ($<1\times10^{-3}$).

References

[1] L. F. Keyser, J. Phys. Chem. **92**, 1193 (1988).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] L. F. Keyser, K. Y. Choo, and M. T. Leu, Int. J. Chem. Kinet. **17**, 1169 (1985).

$HO + H_2O_2 \rightarrow H_2O + HO_2$

$\Delta H° = -130.2$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=1.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=2.9\times10^{-12}\exp(-160/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–460 K.

Reliability

$\Delta\log k=\pm0.1$ at 298 K.

$\Delta(E/R)=\pm100$ K.

Comments on Preferred Values

There are a number of studies in excellent agreement on the value of the rate coefficient.[1-7] The recommended expression is that derived by Kurylo *et al.*,[7] from a least-squares fit to the data in Refs. 2–7, and is identical to our previous evaluation, IUPAC, 1992.[8]

References

[1] G. L. Vaghjiani, A. R. Ravishankara, and N. Cohen, J. Phys. Chem. **93** 7833 (1989).

[2] U. C. Sridharan, B. Reimann, and F. Kaufman, J. Chem. Phys. **73**, 128 (1980).

[3] L. F. Keyser, J. Phys. Chem. **84**, 1659 (1980).

[4] P. H. Wine, D. H. Semmes, and A. R. Ravishankara, J. Phys. Chem. 7 4390 (1981).

[5] F. Temps and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **86**, 11 (1982).

[6] W. J. Marinelli and H. S. Johnston, J. Chem. Phys. **77**, 1225 (1982).

[7] M. J. Kurylo, J. L. Murphy, G. S. Haller, and K. D. Cornett, Int. J. Chen Kinet. **14**, 1149 (1982).

[8] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + O_3 \rightarrow HO_2 + O_2$

167.4 kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

6.7×10^{-14} cm^3 molecule^{-1} s^{-1} at 298 K.

1.9×10^{-12} exp(−1000/T) cm^3 molecule^{-1} s^{-1} over the temperature range 220–450 K.

Reliability

Δlog k = ±0.15 at 298 K.

Δ(E/R) = ±300 K.

Comments on Preferred Values

There is good agreement among the various studies of k. The recommended value for E/R is the mean of the values of Anderson and Kaufman,[1] Ravishankara *et al.*,[2] and Smith *et al.*[3] The recommended value of k at 298 K is the mean of values from these studies plus those of Kurylo[4] and Zahniser and Howard.[5] The pre-exponential factor is derived from the recommended values of E/R and k at 298 K. The preferred values are identical to our previous evaluation, IUPAC, 1992.[6]

References

[1] J. G. Anderson and F. Kaufman, Chem. Phys. Lett. **19**, 483 (1973).

[2] A. R. Ravishankara, P. H. Wine, and A. O. Langford, J. Chem. Phys. **70**, 984 (1979).

[3] C. A. Smith, L. T. Molina, J. J. Lamb, and M. J. Molina, Int. J. Chem. Kinet. **16**, 41 (1984).

[4] M. J. Kurylo, Chem. Phys. Lett. **23**, 467 (1973).

[5] M. S. Zahniser and C. J. Howard, J. Chem. Phys. **73**, 1620 (1980).

[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (1)

$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$ (2)

$\Delta H°(1) = \Delta H°(2) = -165.5$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

k_1 = 1.6×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.

k_2 = 5.2×10^{-32} [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.

k_2 = 4.5×10^{-32} [O_2] cm^3 molecule^{-1} s^{-1} at 298 K.

k_1 = 2.2×10^{-13} exp(600/T) cm^3 molecule^{-1} s^{-1} over the temperature range 230–420 K.

k_2 = 1.9×10^{-33} [N_2] exp(980/T) cm^3 molecule^{-1} s^{-1} over the temperature range 230–420 K.

In the presence of H_2O the expressions for k_1 and k_2 should be multiplied by the factor {1+1.4×10^{-21} [H_2O] exp(2200/T)}.

Reliability

Δlog k_1=Δlog k_2=0.15 at 298 K.

Δ(E_1/R) = ±200 K.

Δ(E_2/R) = ±300 K.

Comments on Preferred Values

Although no new data have been published since our last evaluation, the data have been reviewed by Wallington *et al.*[1] who recommend use of the preferred values given here which are also identical with the values derived by Kircher and Sander.[2]

At temperatures close to 298 K, the reaction proceeds by two channels, one bimolecular and the other termolecular. The preferred values for k_1 are based on the work of Cox and Burrows,[3] Kircher and Sander,[2] Thrush and Tyndall,[4] Takacs and Howard,[5] Kurylo *et al.*,[6] and Lightfoot *et al.*[7] The work of Kurylo *et al.*[6] and of Lightfoot *et al.*[7] has confirmed quantitatively the effects of pressure previously observed by Kircher and Sander[2] and Simonaitis and Heicklen.[8] The recommendations for k_2 are based on the work of these authors, the temperature coefficient of k_2 being taken from Lightfoot *et al.*[7] and Kircher and Sander.[2] At higher temperatures, $T > 600$ K, Hippler *et al.*[9] and Lightfoot *et al.*[7] observe a sharp change in the temperature coefficient. The values of k obtained by Crowley *et al.*[10] in experiments primarily aimed at characterizing the UV absorption spectrum are in good agreement with the recommended expression for k.

There have been no recent experimental studies to check the marked effect of H_2O on the rate coefficient, but the work of Andersson *et al.*[11] shows that CH_3OH has a similar effect, suggesting that it is typical of strongly polar hydrogen bonding species. Mozurkewich and Benson[12] have considered the effect theoretically and conclude that the negative temperature dependence, the pressure dependence, and the observed isotope effects can most reasonably be explained in terms of a cyclic hydrogen bonded, H_2OHO_2, intermediate to alternative structures suggested by others.

Sahetchian *et al.*[13] reported the formation of H_2 (~10% at 500 K) in the system but this is contrary to earlier evidence of Baldwin *et al.*[14] and the more recent and careful study of Stephens *et al.*[15] who find less than 0.01 fractional contribution from the channel leading to $H_2 + 2O_2$.

Keyser *et al.*[16] have measured a yield of $O_2(b^1\Sigma_g^+)$ of $<3\times10^{-2}$ per HO_2 consumed.

References

[1] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).
[2] C. C. Kircher and S. P. Sander, J. Phys. Chem. **88**, 2082 (1984).
[3] R. A. Cox and J. P. Burrows, J. Phys. Chem. **83**, 2560 (1979).
[4] B. A. Thrush and G. S. Tyndall, Chem. Phys. Lett. **92**, 232 (1982).
[5] G. A. Takacs and C. J. Howard, J. Phys. Chem. **90**, 687 (1986).
[6] M. J. Kurylo, P. A. Ouellette, and A. H. Laufer, J. Phys. Chem. **90**, 437 (1986).
[7] P. D. Lightfoot, B. Veyret, and R. Lesclaux, Chem. Phys. Lett. **150**, 120 (1988).
[8] R. Simonaitis and J. Heicklen, J. Phys. Chem. **86**, 3416 (1982).
[9] H. Hippler, J. Troe, and J. Willner, J. Chem. Phys. **93**, 1755 (1990).
[10] J. N. Crowley, F. G. Simon, J. P. Burrows, G. K. Moortgat, M. E. Jenkin, and R. A. Cox, J. Photochem. Photobiol. A: Chem. **60**, 1 (1991).
[11] B. Y. Andersson, R. A. Cox, and M. E. Jenkin, Int. J. Chem. Kinet. **20**, 283 (1988).
[12] M. Mozurkewich and S. W. Benson, Int. J. Chem. Kinet. **17**, 787 (1985).
[13] K. A. Sahetchian, A. Heiss, and R. Rigny, Can. J. Chem. **60**, 2896 (1982).
[14] R. R. Baldwin, C. E. Dean, M. R. Honeyman, and R. W. Walker, J. Chem. Soc. Faraday Trans. 1, **80**, 3187 (1984).
[15] S. L. Stephens, J. W. Birks, and R. J. Glinski, J. Phys. Chem. **93**, 8384 (1989).
[16] L. F. Keyser, K. Y. Choo, and M. T. Leu, Int. J. Chem. Kinet. **17**, 1169 (1985).

$HO_2 + O_3 \rightarrow HO + 2O_2$

$\Delta H^\circ = -118.0$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=2.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.4\times10^{-14}\exp(-600/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability

$\Delta\log k = \pm0.2$ at 298 K.

$\Delta(E/R) = {}^{+500\text{ K}}_{-100\text{ K}}$.

Comments on Preferred Values

A number of studies[1–4] are in close agreement on the value of k at 298 K, but there is some divergence on the temperature coefficient of k. The studies of Sinha *et al.*[3] and Wang *et al.*[4] both agree that k exhibits non-Arrhenius behavior, apparently approaching a constant value of approximately 1×10^{-15} cm^3 molecule^{-1} s^{-1} at $T<250$ K. There are experimental difficulties in working at these temperatures and this finding[3,4] is not incorporated in our recommendation without further confirmation. At higher temperature the results from these two studies[3,4] diverge, giving values of k differing by nearly a factor of 2 at 400 K. We therefore limit the temperature range of our recommendation to $T<350$ K until this discrepancy is resolved.

The preferred values for the range 250–350 K are based on the results of Zahniser and Howard[1] and Wang *et al.*[4] For modeling at temperatures in the range 200–250 K a value of $k=1.2\times10^{-15}$ cm^3 molecule^{-1} s^{-1} should be used. The preferred values are identical to our previous evaluation, IUPAC, 1992.[5]

Isotopic exchange studies[6] of the reaction between $H^{18}O_2$ and O_3 show that at room temperatures the reaction proceeds almost exclusively by H atom transfer rather than by transfer of an oxygen atom. Moreover there is little change in this finding with temperature over the range 226–355 K,[6] indicating that any curvature on the Arrhenius plot cannot be due to competition between these two reaction paths.

References

[1] M. S. Zahniser and C. J. Howard, J. Chem. Phys. **73**, 1620 (1980).
[2] E. R. Manzanares, M. Suto, L. C. Lee, and D. Coffey Jr., J. Chem. Phys. **85**, 5027 (1986).
[3] A. Sinha, E. R. Lovejoy, and C. J. Howard, J. Chem. Phys. **87**, 2122 (1987).
[4] X. Wang, M. Suto, and L. C. Lee, J. Chem. Phys. **88**, 896 (1988).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).
[6] D. D. Nelson, Jr. and M. S. Zahniser, J. Phys. Chem. **98**, 2101 (1994).

$H_2O + h\nu \rightarrow$ products

Primary photochemical transitions

Reactions	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$H_2O + h\nu \rightarrow H_2 + O(^3P)$ (1)	491.0	243
$\rightarrow H + HO$ (2)	499.1	239
$\rightarrow H_2 + O(^1D)$ (3)	680.7	176

No new data have been published since our last evaluation.

Preferred Values

λ/nm	10^{20} σ/cm^2	ϕ_2
175.5	263	1.0
177.5	185	1.0
180.0	78	1.0
182.5	23	1.0
185.0	5.5	1.0
186.0	3.1	1.0
187.5	1.6	1.0
189.3	0.70	1.0

Comments on Preferred Values

Water vapor has a continuous spectrum between 175 and 190 nm; the cross-section decreases rapidly towards longer wavelengths. The cross-section data from four studies[1-4] are in reasonable agreement. None of these studies report numerical data. The preferred values of the absorption cross section are taken from the review of Hudson,[5] and were obtained by drawing a smooth curve through the data of Schurgers and Welge,[4] Watanabe and Zelikoff,[1] and Thompson *et al.*[2]

On the basis of the nature of the spectrum and the results of Chou *et al.*[6] on the photolysis of HTO, it is assumed that over the wavelength region 175–190 nm, reaction (2) is the only primary process and that $\phi_2 = 1.0$.[7]

These recommendations are identical to our previous evaluation, IUPAC, 1992.[8]

References

[1] K. Watanabe and M. Zelikoff, J. Opt. Soc. Am. **43**, 753 (1953).

[2] B. A. Thompson, P. Harteck, and R. R. Reeves, J. Geophys. Res. **68**, 6431 (1963).

[3] A. H. Laufer and J. R. McNesby, Can. J. Chem. **43**, 3487 (1965).

[4] M. Schurgers and K. H. Welge, Z. Naturforsch. **23**, 1508 (1968).

[5] R. D. Hudson, Can J. Chem. **52**, 1465 (1974).

[6] C. C. Chou, J. G. Lo, and F. S. Rowland, J. Chem. Phys. **60**, 1208 (1974).

[7] R. S. Dixon, Radiat. Res. Rev. **2**, 237 (1970).

[8] IUPAC, Supplement IV, 1992 (see references in Introduction).

$H_2O_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions	$\Delta H°$/kJ · mol^1	$\lambda_{threshold}$/nm
$H_2O_2 + h\nu \rightarrow HO + HO$ (1)	215	557
$\rightarrow H_2O + O(^1D)$ (2)	333	359
$\rightarrow H + HO_2$ (3)	369	324
$\rightarrow HO + HO(^2\Sigma)$ (4)	606	197

Quantum yield data

$(\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4)$

Measurement	Wavelength Range/nm	Reference	Comments
$\phi = 1.0$	253.7	Volman, 1963[1]	(a)
$\phi_1 = 1.04 \pm 0.18$	248	Vaghjiani and Ravishankara, 1990[2]	(b)
$\phi_2 < 0.002$	248		
$\phi_3 < 0.0002$	248		
$\phi_1 = 1.01 \pm 0.17$	222	Vaghjiani *et al.*, 1992[3]	(c)
$\phi_2 < 0.002$	222		
$\phi_3 = 0.024 \pm 0.012$	222		
$\phi_1 = 0.79 \pm 0.12$	248	Schiffman *et al.*, 1993[4]	(d)

Comments

(a) Based on a measured overall quantum yield for H_2O_2 removal of $\phi(-H_2O_2)=1.7\pm0.4$ and the assumed mechanism, $H_2O_2 + h\nu \rightarrow 2HO$, $HO + H_2O_2 \rightarrow H_2O + HO_2$, and $2HO_2 \rightarrow H_2O_2 + O_2$. This interpretation has been criticized by Greiner.[5]

(b) Photolysis of flowing mixtures of $H_2O_2-H_2O-N_2$ (or He) and of $O_3-H_2O-N_2$ (or He) at 298 K. H_2O_2 and O_3 were determined by UV absorption at 213.9 nm or 228.8 nm. Quantum yield of HO formation from $H_2O_2-H_2O$ mixture was measured relative to that from O_3-H_2O mixture. These relative yields were placed on an absolute basis using the known quantum yield of HO radical production from the photolysis of O_3-H_2O mixtures at 248 nm, taken as $\phi(HO)=1.73\pm0.09$.[2,6] O and H yields were determined by resonance fluorescence.

(c) Pulsed laser photolysis of $H_2O_2-N_2$ or SF_6 mixtures at 222 nm and 248 nm. [HO] monitored by LIF. The quantum yield of HO production at 248 nm was assumed to be 2.0 and the value at 222 nm was determined from this and the relative HO yields at the two wavelengths. H atom concentrations were monitored by resonance fluorescence. The quantum yield was determined by reference to CH_3SH photolysis at 193 nm. $O(^3P)$ atom formation was investigated using resonance fluorescence but only a very small signal was detected, possibly due to secondary chemistry.

(d) Pulsed laser photolysis of H_2O_2 mixtures. Energy, and hence number of photons, of laser pulse absorbed determined by calorimetry. HO concentrations were monitored by infrared absorption using a color center dye-laser (2.35–3.40 μm) and interferometer for wavelength measurement. Absolute HO radical concentrations were obtained using integrated absorption cross-sections measured in the same laboratory.[7]

Preferred Values

λ/nm	$10^{20}\ \sigma/cm^2$	ϕ_1	λ/nm	$10^{20}\ \sigma/cm^2$	ϕ_1
190	67.2		275	2.6	1.0
195	56.3		280	2.0	1.0
200	47.5		285	1.5	1.0
205	40.8		290	1.2	1.0
210	35.7		295	0.90	1.0
215	30.7		300	0.68	1.0
220	25.8	1.0	305	0.51	1.0
225	21.7	1.0	310	0.39	1.0
230	18.2	1.0	315	0.29	1.0
235	15.0	1.0	320	0.22	1.0
240	12.4	1.0	325	0.16	1.0
245	10.2	1.0	330	0.13	1.0
250	8.3	1.0	335	0.10	1.0
255	6.7	1.0	340	0.07	1.0
260	5.3	1.0	345	0.05	1.0
265	4.2	1.0	350	0.04	1.0
270	3.3	1.0			

Comments on Preferred Values

There have been no new measurements of the absorption cross-sections and our recommendations are unchanged from our previous evaluation, IUPAC, 1992.[8] The preferred values are the means of those determined by Lin *et al.*,[9] Molina and Molina,[10] Nicovich and Wine,[11] and Vaghjiani and Ravishankara.[12] These agree with the earlier values of Holt *et al.*[13] The absorption cross-sections have also been measured at other temperatures by Troe[14] (220–290 nm at 600 K and 1100 K) and by Nicovich and Wine[11] (260–250 nm, 200–400 K). Both Nicovich and Wine[11] and Troe[14] have expressed their results in an analytical form.

It has long been assumed that channel (1) is the only significant primary photochemical channel at $\lambda > 200$ nm. There are measurements by Vaghjiani and Ravishankara[2] and Vaghjiani *et al.*[3] at 248 nm and 222 nm which support this at these wavelengths. However, measurements at 193 nm by Vaghjiani *et al.*[3] show a decline in the HO radical quantum yield (1.51 relative to an assumed value of 2 at 248 nm) with a growth in the H atom quantum yield, a feature previously observed by Gerlach-Meyer *et al.*[15] The results of Schiffman *et al.*[4] also agree well with this relative change in HO radical production in going from 248 nm to 193 nm. However, Schiffman *et al.*[4] obtain much lower absolute values for the quantum yield of HO radical production than obtained by Vaghjiani and Ravishankara.[2]

The evidence therefore indicates that there is a decline in the relative importance of channel (1) in going from 248 nm to 193 nm but the point of onset of this decline and its form are uncertain. Furthermore, the reason for the difference in the absolute values of the quantum yield between the studies of Schiffman *et al.*[4] and Vaghjiani and Ravishankara[2] is unclear; further work is urgently required to clarify this.

Provisionally we continue to recommend the use of a quantum yield of 2 for HO radical production ($\phi_1=1.0$) at $\lambda > 220$ nm.

References

[1] D. H. Volman, J. Chem. Phys. **17**, 947 (1949); Adv. Photochem. **1**, 43 (1963).

[2] G. L. Vaghjiani and A. R. Ravishankara, J. Chem. Phys. **92**, 996 (1990).

[3] G. L. Vaghjiani, A. A. Turnipseed, R. F. Warren, and A. R. Ravishankara, J. Chem. Phys. **96**, 5878 (1992).

[4] A. Schiffman, D. D. Nelson, Jr., and D. J. Nesbitt, J. Chem. Phys. **98**, 6935 (1993).

[5] N. R. Greiner, J. Chem. Phys. **45**, 99 (1966).

[6] P. H. Wine and A. R. Ravishankara, Chem. Phys. **69**, 365 (1982).

[7] D. D. Nelson, Jr., A. Schiffman, and D. J. Nesbitt, J. Chem. Phys. **90**, 5455 (1989).

[8] IUPAC, Supplement IV, 1992 (see references in Introduction).

[9] C. L. Lin, N. K. Rohatgi, and W. B. DeMore, Geophys. Res. Lett. **5**, 113 (1978).

[10] L. T. Molina and M. J. Molina, J. Photochem. **15**, 97 (1981).

[11] J. M. Nicovich and P. H. Wine, J. Geophys. Res. **93**, 2417 (1988).

[12] G. L. Vaghjiani and A. R. Ravishankara, J. Geophys. Res. **94**, 3487 (1989).

[13] R. B. Holt, C. K. McLane, and O. Oldenberg, J. Chem. Phys. **16**, 225, 638 [erratum] (1948).

[14] J. Troe, Helv. Chim. Acta **55**, 205 (1972).

[15] V. Gerlach-Meyer, E. Linnebach, K. Kleinermanns, and J. Wolfrum, Chem. Phys. Lett. **133**, 113 (1987).

4.3. Nitrogen Species

$O + NO + M \rightarrow NO_2 + M$

$\Delta H^\circ = -306.2$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.7\times10^{-32}\ (T/300)^{-(1.41\pm0.02)}$ [Ar]	300–1341	Yarwood *et al.*, 1991[1]	(a)
Reviews and Evaluations			
$1.0\times10^{-31}\ (T/300)^{-1.6}$ [N_2]	200–300	IUPAC, 1992[2]	(b)
$9.0\times10^{-32}\ (T/300)^{-1.5}$ [air]	200–300	NASA, 1994[3]	(c)

Comments

(a) Two experimental techniques were employed. Over the temperature range 300–1000 K, flash photolysis of NO with light from a N_2 discharge lamp was carried out in a temperature-controlled quartz cell. $O(^3P)$ atoms were monitored by resonance fluorescence and the total pressure varied between 50 and 300 Torr. A flash photolysis-shock tube technique was employed between 915 and 1341 K at 30 Torr total pressure. $O(^3P)$ atoms were detected by atomic resonance absorption spectroscopy. Collisional efficiencies $\beta_c = 0.29$, 0.26, 0.18, and 0.16 were derived at 300, 400, 1000, and 2000 K, respectively. In the theoretical analysis, recombination into the $X(^2A_2)$, $A(^2B_2)$, and $C(^2A_2)$ states of NO_2 were taken into account.

(b) Based on the experiments of Ref. 4.

(c) Based on the experiments of Ref. 4 and their reanalysis[4] of the data from Ref. 5 and measurements from Ref. 1.

Preferred Values

$k_0 = 1.0\times10^{-31}\ (T/300)^{-1.6}\ [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_0 = \pm0.10$ at 298 K.

$\Delta n = \pm0.3$.

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.[2] The recent measurements by Yarwood *et al.*[1] at the lowest temperatures are consistent with those recommended in this evaluation.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 3.0\times10^{-11}\ (T/300)^{0.3}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–1500 K.

Reliability

$\Delta\log k_\infty = \pm0.3$.

$\Delta n = \pm0.3$.

Comments on Preferred Values

The preferred values are based on the relative rate measurements of Ref. 6. A reconfirmation by an absolute rate measurement is required. A broadening factor $F_c = 0.85$ at 300 K was estimated, which would correspond to an estimated temperature dependence of $F_c = \exp(-T/1850)$. These preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] G. Yarwood, J. W. Sutherland, M. A. Wickramaaratchi, and R. B. Klemm, J. Phys. Chem. **95**, 8771 (1991).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] M. Schieferstein, K. Kohse-Höinghaus, and F. Stuhl, Ber. Bunsenges. Phys. Chem. **87**, 361 (1983).

[5] D. A. Whytock, J. V. Michael, and W. A. Payne, Chem. Phys. Lett. **42**, 466 (1976).

[6] H. Hippler, C. Schippert, and J. Troe, Int. J. Chem. Kinet. **Symp. 1**, 27 (1975).

$O + NO_2 \rightarrow O_2 + NO$

$\Delta H° = -192.2$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 9.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.5 \times 10^{-12} \exp(120/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–350 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta(E/R) = +120$ K.

Comments on Preferred Values

The preferred value at 298 K is the average of the values reported by Ongstad and Birks,[1] Geers-Müller and Stuhl,[2] Davis *et al.*,[3] Bemand *et al.*,[4] and Slanger *et al.*[5] The recommended temperature dependence results from a least-squares fit to the data of Ongstad and Birks,[6] Geers-Müller and Stuhl[2] and Davis *et al.*,[3] and the preexponential factor has been adjusted to fit the preferred value of k(298 K). The preferred values are identical to our previous evaluation, IUPAC, 1992.[7]

References

[1] A. P. Ongstad and J. W. Birks, J. Chem. Phys. **81**, 3922 (1984).

[2] R. Geers-Müller and F. Stuhl, Chem. Phys. Lett. **135**, 263 (1987).

[3] D. D. Davis, J. T. Herron, and R. E. Huie, J. Chem. Phys. **58**, 530 (1973).

[4] P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 2, **70**, 564 (1974).

[5] T. G. Slanger, B. J. Wood, and G. Black, Int. J. Chem. Kinet. **5**, 615 (1973).

[6] A. P. Ongstad and J. W. Birks, J. Chem. Phys. **85**, 3359 (1986).

[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O + NO_2 + M \rightarrow NO_3 + M$

$\Delta H° = -208.7$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 9.0 \times 10^{-32}(T/300)^{-2.0}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.10$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are from relative rate data.[1] Absolute rate measurements are required. Changes of the reference rate constant $k(O + NO_2 \rightarrow O_2 + NO)$ from the originally used value of 9.3×10^{-12} cm^3 molecule^{-1} s^{-1} to 9.7×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (this evaluation) does not influence the preferred value.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

See comments on k_0.

Intermediate Falloff Range

A broadening of the falloff curve with F_c (300 K) $= 0.8$ and an estimated temperature dependence $F_c = \exp(-T/1300)$ has to be taken into account. The preferred k_0 and k_∞ values depend on the F_c value chosen. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.[2]

References

[1] CODATA, 1980 (see references in Introduction).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O + NO_3 \rightarrow O_2 + NO_2$

$\Delta H^\circ = -289.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is that reported by Canosa-Mas *et al.*,[1] which is the only direct measurement of this rate coefficient. The earlier relative rate value of Graham and Johnston[2] is consistent with the preferred value, taking into account the experimental uncertainties. The temperature dependence is probably near zero by analogy with the reaction of $O(^3P)$ atoms with NO_2. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.[3]

References

[1] C. E. Canosa-Mas, P. J. Carpenter, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **85**, 697 (1989).

[2] R. A. Graham and H. S. Johnston, J. Phys. Chem. **82**, 254 (1978).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O(^1D) + N_2 \rightarrow O(^3P) + N_2$

$\Delta H^\circ = -189.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(2.6 \pm 0.3) \times 10^{-11}$	296	Shi and Barker, 1990[1]	(a)
Reviews and Evaluations			
$1.8 \times 10^{-11} \exp(107/T)$	200–350	IUPAC, 1992[2]	(b)
$1.8 \times 10^{-11} \exp(110/T)$	200–350	NASA, 1994[3]	(b)

Comments

(a) The kinetics of deactivation of $O_2(^1\Sigma_g^+)$ were studied by time-resolved emission from $O_2(^1\Sigma_g^+)$ at 762 nm. $O_2(^1\Sigma_g^+)$ was produced by reaction of $O(^1D)$ atoms with O_2 following laser flash photolysis of O_3. The effect of N_2 (and other quenchers) on the initial fluorescence intensity gives the $O(^1D)$ atom deactivation rate coefficient relative to that for O_2. The rate coefficient for the reaction of $O(^1D)$ atoms with O_2 (this evaluation) is used to determine k.

(b) Based on the measurements of Amimoto *et al.*,[4] Brock and Watson,[5] Wine and Ravishankara,[6] and Streit *et al.*[7]

Preferred Values

$k = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.8 \times 10^{-11} \exp(107/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–350 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The relative rate data of Shi and Barker[1] are in excellent agreement with the earlier studies,[4–7] and there is no change in the recommendation. The preferred value at room temperature is the average of the results of Amimoto *et al.*,[4] Brock and Watson,[5] Wine and Ravishankara,[6] and Streit *et al.*,[7] all of which are in close agreement. The temperature dependence of Streit *et al.*[7] is accepted, and the preexponential factor has been adjusted to fit the preferred room temperature value. The preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] J. Shi and J. R. Barker, Int. J. Chem. Kinet. **22**, 1283 (1990).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] S. T. Amimoto, A. P. Force, R. G. Gulotty, Jr., and J. R. Wiesenfield, J. Chem. Phys. **71**, 3640 (1979).

[5] J. C. Brock and R. T. Watson, results presented at the NATO Advanced Study Institute on Atmospheric Ozone, Portugal, 1979; see G. K. Moortgat's review in Report No. FAA-EE-80-2 (1980).

[6] P. H. Wine and A. R. Ravishankara, Chem. Phys. Lett. **77**, 103 (1981).

[7] G. E. Streit, C. J. Howard, A. L. Schmeltekopf, J. A. Davidson, and H. I. Schiff, J. Chem. Phys. **65**, 4761 (1976).

$$
\begin{aligned}
O(^1D) + N_2O &\rightarrow N_2 + O_2 \quad &(1)\\
&\rightarrow 2NO \quad &(2)\\
&\rightarrow O(^3P) + N_2O \quad &(3)
\end{aligned}
$$

$\Delta H°(1) = -521.0\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta H°(2) = -340.4\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta H°(3) = -189.7\ \mathrm{kJ \cdot mol^{-1}}$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Branching Ratios			
$k_2/k = 0.61 \pm 0.08$	296	Cantrell, Shetter, and Calvert, 1994[1]	(a)
Reviews and Evaluations			
$k_1 = 4.4 \times 10^{-11}$	200–350	IUPAC, 1992[2]	(b)
$k_2 = 7.2 \times 10^{-11}$	200–350		
$k_3 < 1 \times 10^{-12}$	200–350		
$k_1 = 4.9 \times 10^{-11}$	200–300	NASA, 1994[3]	(b)
$k_2 = 6.7 \times 10^{-11}$	200–350		

Comments

(a) Static photolysis of N_2O-O_3 mixtures at $\lambda > 240$ nm with product analysis by FTIR spectroscopy. The amount of NO formed in reaction (2) was determined from the yield of HNO_3 formed by total oxidation and hydration of NO_x products, corrected for losses to the wall. The value of k_2/k obtained from the experimental data was 0.57 ± 0.08; the value given in the table was obtained by averaging the experimental value with selected literature data.

(b) Based on the measurements of Amimoto *et al.*,[4] Wine and Ravishankara,[5] and Davidson *et al.*[6]

Preferred Values

$k_1 = 4.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–350 K.
$k_2 = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–350 K.
$k_3 < 1 \times 10^{-12}$, independent of temperature over the range 200–350 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.1$ at 298 K.

$\Delta(E_1/R) = (E_2/R) = \pm 100$ K.

Comments on Preferred Values

The data and recommendation for the branching ratio at room temperature of $k_2/k = 0.61 \pm 0.08$ given by Cantrell *et al.*[1] are completely in accord with our previous evaluation ($k_2/k = 0.62 \pm 0.09$).[2] The preferred values for the rate coefficients are therefore unchanged from our previous evaluation, IUPAC, 1992.[2] The values at room temperature are the average of the results of Amimoto *et al.*,[4] Wine and Ravishankara,[5] and Davidson *et al.*,[6] all of which are in close agreement. The temperature independence reported by Davidson *et al.*[6] is accepted.

References

[1] C. A. Cantrell, R. E. Shetter, and J. G. Calvert, J. Geophys. Res. **99**, 3739 (1994).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] S. T. Amimoto, A. P. Force, R. G. Gulotty, Jr., and J. R. Weisenfeld, J. Chem. Phys. **71**, 3640 (1979).
[5] P. H. Wine and A. R. Ravishankara, Chem. Phys. Lett. **77**, 103 (1981).
[6] J. A. Davidson, H. I. Schiff, G. E. Streit, J. R. McAfee, A. L. Schmeltekopf, and C. J. Howard, J. Chem. Phys. **67**, 5021 (1977).

$HO + NH_3 \rightarrow H_2O + NH_2$

$\Delta H° = -49.8\ \mathrm{kJ \cdot mol^{-1}}$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.5 \times 10^{-12} \exp(-925/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–450 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The results of Diau *et al.*[1] are in excellent agreement with the previously recommended Arrhenius expression, which was based on the results of Stuhl,[2] Smith and Zellner,[3] Perry *et al.*,[4] Silver and Kolb,[5] and Stephens.[6] There is no change in the preferred value resulting from the inclusion of the new data of Diau *et al.*[1] The many high temperature studies have been considered by Jeffries and Smith[7] to derive a modified Arrhenius expression over an extended temperature range of $k = 1.58 \times 10^{-17}\, T^{1.8} \exp(-250/T)$ cm^3 molecule^{-1} s^{-1} for the temperature range of 225–2350 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[8]

References

[1] E. W.-G. Diau, T.-L. Tso, and Y.-P. Lee, J. Phys. Chem. **94**, 5261 (1990).
[2] F. Stuhl, J. Chem. Phys. **59**, 635 (1973).
[3] I. W. M. Smith and R. Zellner, Int. J. Chem. Kinet. **Symp. 1**, 341 (1975).
[4] R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. **64**, 3237 (1976).
[5] J. A. Silver and C. E. Kolb, Chem. Phys. Lett. **75**, 191 (1980).
[6] R. D. Stevens, J. Phys. Chem. **88**, 3308 (1984).
[7] J. B. Jeffries and G. P. Smith, J. Phys. Chem. **90**, 487 (1986).
[8] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + HONO \rightarrow H_2O + NO_2$

$\Delta H^\circ = -168.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.8 \times 10^{-12} \exp[(260 \pm 140)/T]$	298–373	Burkholder *et al.*, 1992[1]	(a)
$(7.05 \pm 0.26) \times 10^{-12}$	298		
Reviews and Evaluations			
$1.8 \times 10^{-11} \exp(-390/T)$	280–340	IUPAC, 1992[2]	(b)
$1.8 \times 10^{-11} \exp(-390/T)$	200–300	NASA, 1994[3]	(b)

Comments

(a) Laser flash photolysis system with LIF detection of HO radicals. HO radicals were produced from the 266 nm photolysis of O_3 in the presence of excess H_2O, and HONO was prepared from acidified $NaNO_2$ solution and its concentration, together with that of NO_2, was monitored by *in situ* diode-array spectroscopy. Psuedo first-order decays of OH radicals in excess HONO were measured. The reported error limit is the 95% confidence limit.

(b) Based on the measurements of Jenkin and Cox[4] and Cox *et al.*[5]

Preferred Values

$k = 6.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.7 \times 10^{-12} \exp(260/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–400 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 260$ K.

Comments on Preferred Values

The new direct measurements of this rate coefficient from Burkholder *et al.*[1] agree well with the earlier relative rate determination of Cox *et al.*[5] at 296 K [$k = (6.3 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}], but are higher than the direct measurements of Jenkin and Cox[4] using the molecular modulation technique [$k = (4.5 \pm 1.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K]. The new measurements show a small negative temperature dependence whilst the earlier work[4] gave a positive dependence with an activation energy of 3.2 kJ mol^{-1}. The new measurements have substantially better precision and accuracy and the temperature dependence is consistent with that observed for the analogous reaction of HO radicals with $HONO_2$. The preferred value is a weighted average of the reported values of Cox *et al.*,[5] Jenkin and Cox,[4] and Burkholder *et al.*,[1] at 298 K combined with the temperature dependence of Burkholder *et al.*[1]

References

[1] J. B. Burkholder, A. Mellouki, R. Talukdar, and A. R. Ravishankara, Int. J. Chem. Kinet. **24**, 711 (1992).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] M. E. Jenkin and R. A. Cox, Chem. Phys. Lett. **137**, 548 (1987).
[5] R. A. Cox, R. D. Derwent, and P. M. Holt, J. Chem. Soc. Faraday Trans. 1, **72**, 2031 (1976).

$HO + HONO_2 \rightarrow H_2O + NO_3$ (1)
$\rightarrow [H_2NO_4] \rightarrow H_2O + NO_3$ (2)

$\Delta H°(1) = \Delta H°(2) = -72.4$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 1.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.

See comments for expression to be used under other conditions of temperature and pressure.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

Comments on Preferred Values

There is now understanding of the kinetics and mechanism of this complex reaction. There is general consensus on the following major features of the data: (a) a strong negative temperature dependence below room temperature with a much weaker temperature dependence above room temperature which appears to level off near 500 K, and (b) a small but measurable pressure dependence at room temperature which increases at low temperatures. The pressure dependence from 20–100 Torr and 225–298 K was determined by Margitan and Watson,[1] and Stachnik *et al.*[2] measured rate coefficients over the range 10–730 Torr at 297 K and 248 K. These studies agree on a 50 increase in the rate constant at the highest pressure studied at room temperature and a doubling of the low pressure limit at 240 K.

Lamb *et al.*[3] have proposed a mechanism involving formation of a bound, relatively long-lived, intermediate complex. This mechanism gives a rate coefficient expression which combines a low pressure limiting rate constant (k_1) and a Lindemann-Hinshelwood expression for the pressure dependence. This mechanism has been used in the NASA evaluation,[4] and the expression derived in the NASA panel's analysis[4] has been adopted for the evaluation. The overall rate constant can be expressed as:

$$k = k_1(T) + k_2(M,T)$$

where

$$k_2(M,T) = k_3[M]/(1 + k_3[M]/k_4).$$

The expressions for the elementary rate constants are:

$k_1 = 7.2 \times 10^{-15} \exp(785/T)$ cm^3 molecule^{-1} s^{-1},

$k_3 = 1.9 \times 10^{-33} \exp(725/T)$ cm^6 molecule^{-2} s^{-1}, and

$k_4 = 4.1 \times 10^{-16} \exp(1440/T)$ cm^3 molecule^{-1} s^{-1};

all expressions are valid over the temperature range 220–300 K. This expression has been evaluated for the conditions of 298 K and 1 atm pressure to yield the preferred value given here. The reader is referred to Ref. 4 for a more detailed discussion of this reaction. Bossard *et al.*[5] and Singleton *et al.*[6] have reported a pressure and temperature dependence, respectively, of the rate constant for the related reaction $DO + DNO_3$. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[7]

References

[1] J. J. Margitan and R. T. Watson, J. Phys. Chem. **86**, 3819 (1982).
[2] R. A. Stachnik, L. T. Molina, and M. J. Molina, J. Phys. Chem. **90**, 2777 (1986).
[3] J. J. Lamb, M. Mozurkewich, and S. W. Benson, J. Phys. Chem. **88**, 6441 (1984).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] A. R. Bossard, G. Paraskevopoulos, and D. L. Singleton, Chem. Phys. Lett. **134**, 583 (1987).
[6] D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, J. Phys. Chem. **95**, 694 (1991).
[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + HO_2NO_2 \rightarrow H_2O + O_2 + NO_2$ (1)
$\rightarrow H_2O_2 + NO_3$ (2)

$\Delta H°(1) = -191$ kJ·mol^{-1}
$\Delta H°(2) = -44.9$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2$)

$k=5.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=1.5\times10^{-12}\exp(360/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–340 K.

Reliability
$\Delta\log k=\pm0.2$ at 298 K.
$\Delta(E/R)=^{+300\text{ K}}_{-600\text{ K}}$.

Comments on Preferred Values

The preferred value is based on a least-squares fit to the data of Trevor *et al.*,[1] Smith *et al.*,[2] and Barnes *et al.*[3] Trevor *et al.*[1] studied this reaction from 246–324 K at low pressure (4–15 Torr) and recommended a temperature-independent value, but also reported an Arrhenius expression with $E/R=193\pm194$ K. In contrast, Smith *et al.*[2] report data from 240–340 K at one atmosphere pressure and report a negative temperature dependence with $E/R=-(650\pm30)$ K. It is possible that the difference may be due to the reaction being complex with different temperature dependences at low and at high pressure. The error limits on the recommended E/R value encompass the results of both studies. At 220 K the values deduced from these studies differ by a factor of three. The recent study of Barnes *et al.*,[3] the first study over an extended pressure range, found the rate coefficient to be independent of pressure from 5–300 Torr at 278 K and also report the same value at 295 K (low pressure) and at 268 K (100 Torr He). They also report no change with synthetic air as buffer gas. A TST calculation by Lamb *et al.*[4] suggests that the pressure dependence for this rate coefficient will be much less than that for the corresponding reaction of HO with HNO_3. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[5]

References

[1] P. L. Trevor, G. Black, and J. R. Barker, J. Phys. Chem. **86**, 1661 (1982).
[2] C. A. Smith, L. T. Molina, J. J. Lamb, and M. J. Molina, Int. J. Chem. Kinet. **16**, 41 (1984).
[3] I. Barnes, V. Bastian, K. H. Becker, E. H. Fink, and F. Zabel, Chem. Phys. Lett. **83**, 459 (1981).
[4] J. J. Lamb, M. Mozurkewich, and S. W. Benson, J. Phys. Chem. **88**, 6441 (1984).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + NO + M \rightarrow HONO + M$

$\Delta H^\circ=-209.0$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
5.0×10^{-31} [Ar]	298–422	Zabarnick, 1993[1]	(a)
1.5×10^{-30} [SF_6]	298–430		
3.9×10^{-31} $(T/300)^{-2.4}$ [He]	250–400	Forster *et al.*, 1995[2]	(b)
Reviews and Evaluations			
7.4×10^{-31} $(T/300)^{-2.4}$ [N_2]	200–300	IUPAC, 1992[3]	(c)
7.0×10^{-31} $(T/300)^{-2.6}$ [air]	200–300	NASA, 1994[4]	(d)

Comments

(a) HO radicals were generated by photodissociation of HNO_3 at 248 nm and monitored by LIF at 310 nm. The bath gases Ar (50–400 Torr), N_2 (100 Torr), and SF_6 (50–400 Torr) were employed. Extrapolations were performed with a Lindemann–Hinshelwood expression.

(b) Laser flash photolysis system with saturated LIF detection of HO radicals. Measurements were made over the pressure range 1–110 bar. Falloff extrapolations were carried out with $F_c=0.9$ at 250 K and $F_c=0.8$ at 400 K.

(c) The preferred values have not been changed since 1984, because the data base appears fairly complete and consistency with theoretical analysis was obtained. The new high pressure measurements[2] put the falloff extrapolation on a sounder basis.

(d) The recommended value is a weighted average of the data from Refs. 5–15, with heavy weighting to Ref. 14.

Preferred Values

$k_0=7.4\times10^{-31}(T/300)^{-2.4}[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability
$\Delta\log k_0=\pm0.10$ at 298 K.
$\Delta n=\pm0.5$.

Comments on Preferred Values

The measurements from Refs. 1 and 2 appear consistent with our earlier recommendation,[3] which remains unchanged.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
8.4×10^{-12}	298–422	Zabarnick, 1993[1]	(a)
3.0×10^{-11}	298		
8.0×10^{-11}	430		
4.5×10^{-11}	250–400	Forster *et al.*, 1995[2]	(b)
Reviews and Evaluations			
3.2×10^{-11}	200–400	IUPAC, 1992[3]	(c)
1.5×10^{-11}	200–300	NASA, 1994[4]	(d)

Comments

(a) See comment (a) on k_0. The first value was obtained in M=Ar, while the other values were extrapolated from measurements in M=SF_6.

(b) See comment (b) on k_0.

(c) Based on preliminary data from Ref. 2.

(d) The recommended value is a weighted average of the data of Anastasi and Smith[14] and Anderson *et al.*[9]

Preferred Values

$k_\infty = 4.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta\log k_\infty = \pm0.2$ over the temperature range 200–400 K.

Comments on Preferred Values

The preferred values are from Ref. 2, where a major part of the falloff curves was measured (up to 100 bar of M =He) at 250, 300, and 400 K. Falloff curves are constructed with F_c=0.9 at 250 K and 0.8 at 400 K.

References

[1] S. Zabarnick, Chem. Phys. **171**, 265 (1993).
[2] R. Forster, M. Frost, D. Fulle, H. F. Hamann, H. Hippler, A. Schlepegrell, and J. Troe, J. Chem. Phys. **103**, 2949 (1995).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] J. G. Anderson and F. Kaufman, Chem. Phys. Lett. **16**, 375 (1972).
[6] F. Stuhl and H. Niki, J. Chem. Phys. **57**, 3677 (1972).
[7] C. Morley and I. W. M. Smith, J. Chem. Soc. Faraday Trans. 2, **68**, 1016 (1972).
[8] A. A. Westenberg and N. deHaas, J. Chem. Phys. **57**, 5375 (1972).
[9] J. G. Anderson, J. J. Margitan, and F. Kaufman, J. Chem. Phys. **60**, 3310 (1974).
[10] C. J. Howard and K. M. Evenson, J. Chem. Phys. **61**, 1943 (1974).
[11] G. W. Harris and R. P. Wayne, J. Chem. Soc. Faraday Trans. 1, **71**, 610 (1975).
[12] R. Atkinson, D. A. Hansen, and J. N. Pitts, Jr., J. Chem. Phys. **62**, 3284 (1975).
[13] R. P. Overend, G. Paraskevopoulos, and C. Black, J. Chem. Phys. **64**, 4149 (1976).
[14] C. Anastasi and I. W. M. Smith, J. Chem. Soc. Faraday Trans. 2, **74**, 1056 (1978).
[15] J. P. Burrows, T. J. Wallington, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **79**, 111 (1983).

$HO + NO_2 + M \rightarrow HNO_3 + M$

$\Delta H° = -207.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.5\times10^{-30}\ (T/300)^{-3.0}$ [He]	268–400	Forster *et al.*, 1995[1]	(a)
Reviews and Evaluations			
$2.6\times10^{-30}\ (T/300)^{-2.9}$ [N_2]	200–300	IUPAC, 1992[2]	(b)
$2.6\times10^{-30}\ (T/300)^{-3.2}$ [air]	200–400	NASA, 1994[3]	(c)

Comments

(a) Laser flash photolysis system with saturated LIF detection of HO radicals. Measurements were made between 1 and 150 bar. Falloff curves were constructed with $F_c=0.46$ at 270 K, 0.43 at 300 K, and 0.37 at 400 K.
(b) The data base is large. This evaluation was based on a calculated value of $F_c=0.43$ at 300 K.
(c) The values are from Refs. 4–8. The temperature dependence was based on $(-\langle \Delta E\rangle)=2.3$ kJ mol^{-1} for $M=N_2$.

Preferred Values

$k_0=2.6\times10^{-30}\ (T/300)^{-2.9}\ [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta\log k_0=\pm0.1$ at 298 K.

$\Delta n=\pm0.3$.

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.[2] The new measurements for M=He from Ref. 1 appear consistent with this recommendation.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.7\times10^{-11}\ (T/300)^{-0.6}$	260–400	Forster *et al.*, 1995[1]	(a)
Reviews and Evaluations			
6.0×10^{-11}	200–300	IUPAC, 1992[2]	(b)
$2.4\times10^{-11}\ (T/300)^{-1.3}$	200–300	NASA, 1994[3]	(c)

Comments

(a) See comment (a) for k_0.
(b) Based on preliminary data from Ref. 1.
(c) The recommended values were from a RRKM model of Smith and Golden.[9]

Preferred Values

$k_\infty=6.7\times10^{-11}\ (T/300)^{-0.6}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta\log k_\infty=\pm0.10$ at 298 K.

$\Delta n=\pm0.5$.

Comments on Preferred Values

The preferred values are from the measurements of Ref. 1, which covered the largest part of the falloff curves.

References

[1] R. Forster, M. Frost, D. Fulle, H. F. Hamann, H. Hippler, A. Schlepegrell, and J. Troe, J. Chem. Phys. **103**, 2949 (1995).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] J. G. Anderson, J. J. Margitan, and F. Kaufman, J. Chem. Phys. **60**, 3310 (1974).
[5] C. J. Howard and K. M. Evenson, J. Chem. Phys. **61**, 1943 (1974).
[6] C. Anastasi and I. W. M. Smith, J. Chem. Soc. Faraday Trans. 2, **72**, 1459 (1976).
[7] P. H. Wine, N. M. Kreutter, and A. R. Ravishankara, J. Phys. Chem. **83**, 3191 (1979).
[8] J. P. Burrows, T. J. Wallington, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **79**, 111 (1983).
[9] G. P. Smith and D. M. Golden, Int. J. Chem. Kinet. **10**, 489 (1978).

$HO + NO_3 \rightarrow HO_2 + NO_2$

$\Delta H° = -65.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.22\pm0.35)\times10^{-11}$	298	Becker, Rahman, and Schindler, 1992[1]	(a)
$(2.1\pm1.0)\times10^{-11}$	297	Mellouki *et al.*, 1993[2]	(b)
Reviews and Evaluations			
2.3×10^{-11}	298	IUPAC, 1992[3]	(c)
2.2×10^{-11}	298	NASA, 1994[4]	(d)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO radicals. NO_3 and HO_2 radical concentrations were measured by mass spectrometry. The HO radical time-dependence was followed in the presence of excess NO_3 radical concentrations. The rate coefficients obtained with HO radical production *in situ* from the $H + NO_2$ reaction and with injection of HO radicals from either the $H + NO_2$ or $F + H_2O$ reactions were the same within the experimental errors. A complex kinetic analysis was required to extract the rate coefficients by computer simulation using a complex mechanism, taking account of secondary reactions of the HO_2 radical product. The average value is reported and the cited error refers to precision only.

(b) Discharge flow system with LMR detection of HO and HO_2 radicals and NO_2. The $H + NO_2$ reaction was used to generate HO radicals, and NO_3 radicals were produced by the thermal decomposition of N_2O_5. NO_3 radicals were detected by titration with NO, monitoring the NO_2 product. The rate coefficient was determined by a psuedo first-order analysis with NO_3 in excess over HO. The average value of k is reported.

(c) Mean of the data of Mellouki *et al.*[5] and Boodaghians *et al.*[6]

(d) Weighted average of the data from Refs. 1, 2, 5, and 6.

Preferred Values

$k = 2.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$.

Comments on Preferred Values

The two new measurements[1,2] of this rate constant using the discharge flow technique at room temperature are not in good agreement. The rate coefficient reported by Mellouki *et al.*[2] is in good agreement with the two earlier determinations,[5,6] but less accuracy is claimed. The rate coefficient of Becker *et al.*[1] is a factor of 2 lower and the discrepancy is well outside the claimed accuracy. In all systems corrections for secondary reactions were required, but the reasons for the discrepancies are not clear. The preferred value for k is a simple average of the 4 reported values.[1,2,5,6] In the absence of experimental data a temperature dependence cannot be recommended. Consistent with other radical + radical reactions, a small negative temperature coefficient is expected.

References

[1] E. Becker, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **96**, 776 (1992).

[2] A. Mellouki, R. K. Talukdar, A. M. R. P. Bopegedera, and C. J. Howard, Int. J. Chem. Kinet. **25**, 25 (1993).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

[5] A. Mellouki, G. Le Bras, and G. Poulet, J. Phys. Chem. **92**, 2229 (1988).

[6] R. B. Boodaghians, C. E. Canosa-Mas, P. J. Carpenter, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **84**, 931 (1988).

$HO_2 + NO \rightarrow HO + NO_2$

$\Delta H° = -32.4$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 8.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.7 \times 10^{-12} \exp(240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–500 K.

Reliability
$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred value at 298 K is a mean of the five determinations of Hack *et al.*,[1] Howard,[2] Leu,[3] Howard and Evenson,[4] and Jemi-Alade and Thrush.[5] The value reported by Glaschick-Schimpf *et al.*[6] of 1.1×10^{-11} cm^3 molecule^{-1} s^{-1} is high, but in agreement within the stated uncertainty. The temperature dependence is that reported by Howard[7] for the combined temperature range 232–1271 K, based on high temperature data[7] and the low temperature data of Howard.[2] This temperature dependence measured over a very large temperature range is preferred to that reported by Leu[3] ($E/R = 130$ K) obtained over a much smaller temperature range. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[8]

References

[1] W. Hack, A. W. Preuss, F. Temps, H. Gg. Wagner, and K. Hoyermann, Int. J. Chem. Kinet. **12**, 851 (1980).
[2] C. J. Howard, J. Chem. Phys. **71**, 2352 (1979).
[3] M.-T. Leu, J. Chem. Phys. **70**, 1662 (1979).
[4] C. J. Howard and K. M. Evenson, Geophys. Res. Lett. **4**, 437 (1977).
[5] A. A. Jemi-Alade and B. A. Thrush, J. Chem. Soc. Faraday Trans. **86**, 3355 (1990).
[6] I. Glaschick-Schimpf, A. Leiss, P. B. Monkhouse, U. Schurath, K. H. Becker, and E. H. Fink, Chem. Phys. Lett. **67**, 318 (1979).
[7] C. J. Howard, J. Am. Chem. Soc. **102**, 6937 (1980).
[8] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$

$\Delta H^\circ = -105$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.8 \times 10^{-31} (T/300)^{-3.2} [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability
$\Delta \log k_0 = \pm 0.10$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The latest data of Jemi-Alade and Thrush[1] are consistent with the series of earlier measurements reviewed in Refs. 2 and 3. Refinement of F_c by calculations will lead to minor modifications of k_0.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 4.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability
$\Delta \log k_\infty = \pm 0.2$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

A temperature independent value of k_∞ is chosen in agreement with other reaction systems. Improved falloff extrapolations would require measurements above 1 bar and the use of a calculated value of F_c different from a fixed $F_c = 0.6$. The preferred values of k_0 and k_∞ are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] A. A. Jemi-Alade and B. A. Thrush, J. Chem. Soc. Faraday Trans. **86**, 3355 (1990).
[2] CODATA, 1980 (see references in Introduction).
[3] IUPAC, Supplement III, 1989 (see references in Introduction).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$

$\Delta H° = 105$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.3 \times 10^{-20}$ [N_2] s^{-1} at 298 K.

$k_0 = 5 \times 10^{-6} \exp(-10000/T)$ [N_2] s^{-1} over the temperature range 260–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

More studies of the dissociation reaction appear desirable. By combining the preferred values with the corresponding recombination results, an equilibrium constant of $K_c = 1.8 \times 10^{-27} \exp(10900/T)$ cm^3 molecule^{-1} is obtained, in close agreement with the evaluation of Ref. 1.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 0.34$ s^{-1} at 298 K.

$k_\infty = 2.6 \times 10^{15} \exp(-10900/T)$ s^{-1} over the temperature range 260–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 500$.

Comments on Preferred Values

Because the falloff curves for recombination have been determined more systematically, we have combined the corresponding high-pressure limit for the recombination reaction with the equilibrium constant K_c (see comment to preferred values of k_0) to obtain k_∞. Since $F_c = 0.6$ was used for the falloff extrapolation of the recombination, an even larger value of k_∞ is expected if $F_c = 0.4$ is used.[2] These preferred values of k_0 and k_∞ are identical to our previous evaluation. IUPAC, 1992.[3]

References

[1] NASA Evaluation No. 11, 1994 (see references in Introduction).
[2] CODATA, Supplement I, 1982 (see references in Introduction).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO_2 + NO_3 \rightarrow O_2 + HNO_3$ (1)
$\rightarrow HO + NO_2 + O_2$ (2)

$\Delta H^\circ(1) = -223.4$ kJ·mol^{-1}
$\Delta H^\circ(2) = -15.8$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_1=(1.9\pm0.8)\times10^{-12}$	298	Becker, Rahman, and Schindler, 1992[1]	(a)
$k_2=(2.5\pm0.7)\times10^{-12}$	298		
$(3.0\pm0.7)\times10^{-12}$	297±2	Mellouki *et al.*, 1993[2]	(b)
Branching Ratios			
$k_2/k=1.0^{+0.0}_{-0.3}$	297	Mellouki *et al.*, 1993[2]	(b)
Reviews and Evaluations			
4.3×10^{-12}	298	IUPAC, 1992[3]	(c)
3.5×10^{-12}	298	NASA, 1994[4]	(d)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO radicals. NO_3 and HO_2 radical concentrations were measured by mass spectrometry. The O_2 + CH_2OH reaction was used to generate HO_2 radicals, and NO_3 radicals were produced by the F + HNO_3 reaction. The HO_2 and HO radical time-dependence was monitored in the presence of excess concentrations of NO_3 radicals. The rate coefficient k_1 was inferred from the enhanced loss of HO_2 radicals following the attainment of a quasi-steady state of HO_2 and HO radicals due to secondary reactions of HO radicals with NO_3 radicals reforming HO_2 radicals. Rate coefficients k were obtained by computer simulation using a complex mechanism, taking account of secondary reactions of HO and HO_2 radicals including wall loss. The average values from 10 experiments is reported and the error limits refer to precision only.

(b) Discharge flow system with LMR detection of HO and HO_2 radicals and NO_2. The H + O_2 + M reaction was used to generate HO_2 radicals. NO_3 radicals were produced by three methods: F + HNO_3, Cl + $ClNO_3$, and thermal decomposition of N_2O_5 and detected by titration with NO and monitoring the NO_2 product. NO_3 radicals were in >30 fold excess over HO_2 radicals and C_2F_3Cl was added to scavenge the HO radical product. The rate coefficient k was determined under psuedo first-order conditions. The average value of k was reported with estimated overall accuracy. The branching ratio is based on computer simulation of absolute time-dependencies of HO and HO_2 radicals using a simple mechanism.

(c) Mean of the values from Mellouki *et al.*[5] and Hall *et al.*[6]

(d) Weighted average of data from Mellouki *et al.*,[2,5] Hall *et al.*[6] and Becker *et al.*[1]

Preferred Values

$k=4.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.2$.

Comments on Preferred Values

The two new measurements of this rate constant, using discharge flow techniques at room temperature, are in reasonably good agreement. While the measurement of the overall rate constant (k_1+k_2) by Becker *et al.*[1] is in good agreement with the two earlier determinations of $(4.5\pm1.4)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}[5] and 4.1×10^{-12} cm^3 molecule^{-1} s^{-1},[6] the result of Mellouki *et al.*[2] is 30% lower. The three earlier studies[1,5,6] propose that both channels (1) and (2) occur, but the branching ratio from the HO yields measured by Mellouki *et al.*,[2] which appears to be the most direct determination, suggests near a 100% reaction via the second channel. The preferred value for k is a weighted average of the 4 reported values.[1,2,5,6] No recommendation is made for the branching ratio because of the experimental uncertainties. A temperature dependence was reported by Hall *et al.*,[6] with $k=2.3\times10^{-12}\exp[(170\pm270)/T]$ cm^3 molecule^{-1} s^{-1}, but because of the large uncertainty no recommendation is given. In line with other radical + radical reactions, a small negative temperature coefficient is expected.

References

[1] E. Becker, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **96**, 776 (1992).

[2] A. Mellouki, R. K Talukdar, A. M. R. P. Bopegedera, and C. J. Howard, Int. J. Chem. Kinet. **25**, 25 (1993).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

[5] A. Mellouki, G. Le Bras, and G. Poulet, J. Phys. Chem. **92**, 2229 (1988).

[6] I. W. Hall, R. P. Wayne, R. A. Cox, M. E. Jenkin, and G. D. Hayman, J. Phys. Chem. **92**, 5049 (1988).

$NH_2 + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$<6\times10^{-21}$	296	Tyndall *et al.*, 1991[1]	(a)
Reviews and Evaluations			
$<3\times10^{-18}$	298	IUPAC, 1992[2]	(b)
$<6\times10^{-21}$	298	NASA, 1994[3]	(c)

Comments

(a) Photolysis of NH_3 in the presence and absence of excess O_2. NO, NO_2, and N_2O products were measured by FTIR spectroscopy. The upper limit to the rate coefficient was based on a computer simulation with a complex reaction mechanism.

(b) Based on the measurements of Lesclaux and Demissy,[4] Cheskis and Sarkisov,[5] Patrick and Golden,[6] Lozovsky *et al.*,[7] and Michael *et al.*[8]

(c) Based on the data of Tyndall *et al.*[1]

Preferred Values

$k=<6\times10^{-21}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This reaction has several energetically feasible product channels, including NO + H_2O and HNO + HO. The new measurements of Tyndall *et al.*[1] of the upper limit to the rate coefficient for all channels leading directly or indirectly to NO, NO_2 and N_2O confirm earlier conclusions that the reaction is very slow,[4–8] and reduces the upper limit by three orders of magnitude. Systematic uncertainties in the system were identified which would cause an overestimate of the rate coefficient. The new upper limit is recommended, making this reaction unimportant in the atmosphere.

References

[1] G. S. Tyndall, J. J. Orlando, K. E. Nickerson, C. A. Cantrell, and J. G. Calvert, J. Geophys. Res. **96**, 20761 (1991).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] R. Lesclaux and M. Demissy, Nouv. J. Chim. **1**, 443 (1977).

[5] S. G. Cheskis and O. M. Sarkisov, Chem. Phys. Lett. **62**, 72 (1979).

[6] R. Patrick and D. M. Golden, J. Phys. Chem. **88**, 491 (1984).

[7] V. A. Lozovsky, M. A. Ioffe, and O. M. Sarkisov, Chem. Phys. Lett. **110**, 651 (1984).

[8] J. V. Michael, R. B. Klemm, W. D. Brobst, S. R. Bosco, and D. F. Nava, J. Phys. Chem. **89**, 3335 (1985).

$NH_2 + O_3 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=1.7\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=4.9\times10^{-12}\exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–380 K.

Reliability

$\Delta\log k=\pm0.5$ at 298 K.

$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The preferred value is taken as the average of the results reported by Kurasawa and Lesclaux,[1] Bulatov *et al.*,[2] Hack *et al.*,[3] Patrick and Golden,[4] and Cheskis *et al.*[5] The temperature dependence averages the values reported by Kurasawa and Lesclaux,[1] Hack *et al.*,[3] and Patrick and Golden.[4] Although the products of this reaction have not been determined, the most likely process is abstraction of an oxygen atom by NH_2 to give $NH_2O + O_2$. While it has been *al.*[2,3] that NH_2 may be regenerated by reaction of [illegible] with O_3, the study of Patrick and Golden[4] indicates the reaction must be slow. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[6]

References

[1] [illegible]awa and R. Lesclaux, Chem. Phys. Lett. **72**, 437 (1980).
[2] Bulatov, A. A. Buloyan, S. G. Cheskis, M. Z. Kozliner, O. M. Sarkisov, and A. I. Trostin, Chem. Phys. Lett. **74**, 288 (1980).
[3] W. Hack, O. Horie, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **85**, 72 (1981)
[4] R. Patrick and D. M. Golden, J. Phys. Chem. **88**, 491 (1984).
[5] S. G. Cheskis, A. A. Iogansen, O. M. Sarkisov, and A. A. Titov, Chem. Phys. Lett. **120**, 45 (1985).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$$
\begin{aligned}
\mathbf{NH_2 + NO} &\rightarrow \mathbf{N_2 + H_2O} && \mathbf{(1)}\\
&\rightarrow \mathbf{N_2H + HO} && \mathbf{(2)}\\
&\rightarrow \mathbf{N_2 + H + HO} && \mathbf{(3)}
\end{aligned}
$$

[illegible] $517.5\ \text{kJ}\cdot\text{mol}^{-1}$
[illegible] $18.4\ \text{kJ}\cdot\text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2+k_3$)

1.6×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K.
$1.6\times10^{-11}\exp(T/298)^{-1.5}$ cm^3 molecule^{-1} s^{-1} over the temperature range 210–500 K.
$(k_2+k_3)/k=0.1$ at 298 K.

Reliability
$\Delta\log k=\pm0.2$ at 298 K.
$\Delta n=\pm0.5$.
$\Delta(k_2+k_3)/k=\pm0.03$ at 298 K.

Comments on Preferred Values

The preferred value at 298 K is the average of the determinations of Atakan *et al.*[1] and Bulatov *et al.*[2] together with the values reported in Refs. 3–13. The temperature dependence is based on the data below 500 K in the six temperature dependence studies of Silver and Kolb,[5] Stief *et al.*,[6] Lesclaux *et al.*,[12] Hack *et al.*,[13] Atakan *et al.*,[1] and Bulatov *et al.*[2]

The direct measurements of the branching ratio reported by Atakan *et al.*[1] are the basis for the recommendation for $(k_2+k_3)/k$. Other, less direct, rate coefficient ratio determinations are consistent with the value recommended, with the exception of the results of Andresen *et al.*[7] who report that the production of HO dominates; this discrepancy has not been explained. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[14]

References

[1] B. Atakan, A. Jacobs, M. Wahl, R. Weller, and J. Wolfrum, Chem. Phys. Lett. **155**, 609 (1989); B. Atakan, J. Wolfrum, and R. Weller, Ber. Bunsenges Phys. Chem. **94**, 1372 (1990).
[2] V. P. Bulatov, A. A. Ioffe, V. A. Lozovsky, and O. M. Sarkisov, Chem. Phys. Lett. **161**, 141 (1989).
[3] A. R. Whyte and L. F. Phillips, Chem. Phys. Lett. **102**, 451 (1983).
[4] T. Dreier and J. Wolfrum, *20th International Symposium on Combustion, 1984* (The Combustion Institute, Pittsburgh, PA, 1985), pp. 695–702.
[5] J. A. Silver and C. E. Kolb, J. Phys. Chem. **91**, 3713 (1987).
[6] L. J. Stief, W. D. Brobst, D. F. Nava, R. P. Borkowski, and J. V. Michael, J. Chem. Soc. Faraday Trans. 2, **78**, 1391 (1982).
[7] P. Andresen, A. Jacobs, C. Kleinermanns, and J. Wolfrum, *19th International Symposium on Combustion, 1982* (The Combustion Institute, Pittsburgh, PA, 1982), pp. 11–22.
[8] S. Gordon, W. Mulac, and P. Nangia, J. Phys. Chem. **75**, 2087 (1971).
[9] M. Gehring, K. Hoyermann, H. Schacke, and J. Wolfrum, *14th International Symposium on Combustion, 1972* (The Combustion Institute, Pittsburgh, PA, 1973), pp. 99–105.
[10] G. Hancock, W. Lange, M. Lenzi, and K. H. Welge, Chem. Phys. Lett. **33**, 168 (1975).
[11] O. M. Sarkisov, S. G. Cheskis, and E. A. Sviridenkov, Bull. Acad. Sci. USSR, Chem. Ser. **27**, 2336, Eng. Trans. (1978).
[12] R. Lesclaux, P. V. Khe, P. Dezauzier, and J. C. Soulignac, Chem. Phys. Lett. **35**, 493 (1975).
[13] W. Hack, H. Schacke, M. Schröter, and H. Gg. Wagner, *17th International Symposium on Combustion, 1978* (The Combustion Institute, Pittsburgh, PA, 1979), pp. 505–513.
[14] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NH_2 + NO_2 \rightarrow N_2O + H_2$ (1)
$\rightarrow N_2 + H_2O_2$ (2)

$\Delta H^\circ(1) = -378$ kJ·mol^{-1}
$\Delta H^\circ(2) = -355$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 2.0 \times 10^{-11}$ $(T/298)^{-2.0}$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–500 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta n = \pm 0.7$.

Comments on Preferred Values

The preferred value at 298 K is the average of the values from Bulatov *et al.*,[1] Whyte and Phillips,[2] Kurasawa and Leclaux,[3] Xiang *et al.*,[4] and Hack *et al.*[5] The temperature dependence is the average from Refs. 1, 3, and 5. Hack *et al.*,[5] using mass spectrometric analysis, determined that the predominant reaction channel is channel (1) to give N_2O + H_2O, with at least 95% of the reaction proceeding by the channel. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[6]

References

[1] V. P. Bulatov, A. A. Ioffe, V. A. Lozovsky, and O. M. Sarkisov, Chem Phys. Lett. **159**, 171 (1989).
[2] A. R. Whyte and L. F. Phillips, Chem. Phys. Lett. **102**, 451 (1983).
[3] H. Kurasawa and R. Lesclaux, Chem. Phys. Lett. **66**, 602 (1979).
[4] T.-X. Xiang, L. M. Torres, and W. A. Guillory, J. Chem. Phys. **83**, 1623 (1985).
[5] W. Hack, H. Schacke, M. Schröter, and H. Gg. Wagner, *17th International Symposium on Combustion, 1978* (The Combustion Institute, Pittsburgh, PA, 1979), pp. 505–513.
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$2NO + O_2 \rightarrow 2NO_2$

$\Delta H^\circ = -114.1$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 2.0 \times 10^{-38}$ cm^6 molecule^{-2} s^{-1} at 298 K.
$k = 3.3 \times 10^{-39} \exp(530/T)$ cm^6 molecule^{-2} s^{-1} over the temperature range 273–600 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

This evaluation accepts the recommendation given in the evaluation by Baulch *et al.*[1] Olbregts[2] observed non-Arrhenius behavior over the entire temperature range studied and expressed k by a modified Arrhenius expression and also as the sum of two Arrhenius expressions. However, from 250 K to about 600 K the total rate coefficient of Olbregts[2] is in good agreement with the value calculated from the expression recommended here. Olbregts[2] interpreted his results in terms of a multi-step mechanism involving NO_3 or the dimer $(NO)_2$ as intermediates. For atmospheric modeling purposes, the expression recommended here is adequate. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] D. L. Baulch, D. D. Drysdale, and D. G. Horne, *Evaluated Kinetic Data for High Temperature Reactions*, Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System Vol. 2 (Butterworths, London, 1973).
[2] J. Olbregts, Int. J. Chem. Kinet. **17**, 835 (1985).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO + O_3 \rightarrow NO_2 + O_2$

$\Delta H^\circ = -199.8$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.8\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.8\times10^{-12}$ exp($-1370/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 195–304 K.

Reliability

$\Delta\log k = \pm0.08$ at 298 K.

$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

The preferred Arrhenius expression is based on least-squares analysis of the data at and below room temperature reported by Michael *et al.*,[1] Borders and Birks,[2] Lippmann *et al.*,[3] Ray and Watson,[4] and Birks *et al.*,[5] with data at closely spaced temperatures reported by Borders and Birks[2] and Lippmann *et al.*[3] being grouped to give equal weight to each of the five studies. The preferred expression fits these data to within 20%. Only data between 195 and 304 K were used due to the nonlinear Arrhenius behavior observed by Michael *et al.*,[1] Borders and Birks,[2] Birks *et al.*,[5] Clyne *et al.*,[6] and Clough and Thrush.[7] Michael *et al.*,[1] Birks *et al.*,[5] Clyne *et al.*,[6] and Schurath *et al.*[8] have reported individual Arrhenius parameters for each of two primary reaction channels (one to produce NO_2 in the ground electronic state and the other to produce electronically excited NO_2). Earlier room-temperature results of Stedman and Niki[9] and Bemand *et al.*[10] are in good agreement with the preferred value. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[11]

References

[1] J. V. Michael, J. E. Allen, Jr., and W. D. Brobst, J. Phys. Chem. **85**, 4109 (1981).

[2] R. A. Borders and J. W. Birks, J. Phys. Chem. **86**, 3295 (1982).

[3] H. H. Lippmann, B. Jesser, and U. Schurath, Int. J. Chem. Kinet. **12**, 547 (1980).

[4] G. W. Ray and R. T. Watson, J. Phys. Chem. **85**, 1673 (1981).

[5] J. W. Birks, B. Shoemaker, T. J. Leck, and D. M. Hinton, J. Chem. Phys. **65**, 5181 (1976).

[6] M. A. A. Clyne, B. A. Thrush, and R. P. Wayne, Trans. Faraday Soc. **60**, 359 (1964).

[7] P. N. Clough and B. A. Thrush, Trans. Faraday Soc. **63**, 915 (1967).

[8] U. Schurath, H. H. Lippmann, and B. Jesser, Ber. Bunsenges. Phys. Chem. **85**, 807 (1981).

[9] D. H. Stedman and H. Niki, J. Phys. Chem. **77**, 2604 (1973).

[10] P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 2, **70**, 564 (1974).

[11] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO + NO_2 + M \rightarrow N_2O_3 + M$

$\Delta H^\circ = -40.5$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.6\pm0.15)\times10^{-33}$ [He]	208	Smith and Yarwood, 1986[1]	(a)
$(5.5\pm0.8)\times10^{-33}$ [Ar]	208		
$(4.2\pm0.3)\times10^{-33}$ [He]	206	Smith and Yarwood, 1987[2]	(b)
$(6.7\pm0.6)\times10^{-33}$ [Ar]	207		
$(5.0\pm0.4)\times10^{-33}$ [Ne]	203		
$(9.1\pm0.7)\times10^{-33}$ [N_2]	208		
$(13.9\pm1.0)\times10^{-33}$ [CF_4]	208		
$(2.8\pm1.4)\times10^{-33}$ [Ar]	227	Markwalder, Gozel, and van den Bergh, 1993[3]	(c)
$(2.8\pm2.8)\times10^{-15}$ $T^{-(7.7\pm0.8)}$ [Ar]	227–260		

Comments

(a) Partial photolysis of N_2O_3 in equilibrium NO_2-N_2O_4-NO-N_2O_3-He (or Ar) mixtures. The relaxation to equilibrium was monitored by observing the transmittance of a cw CO laser selected to coincide with the ν_1 band of N_2O_3 at 1829.59 cm^{-1}. The total pressure was 190–660 Torr.

(b) Flash photolysis perturbation of NO_2-N_2O_4-N_2O_3 mixtures in excess of NO. N_2O_3 was monitored at the ν_1 band using a CO laser. Pressure was varied between 190–6970 Torr (He), 190–500 Torr (Ar), 248–6970 Torr (Ne), 166–401 Torr (N_2), and 132–441 Torr (CF_4). Falloff curves were extrapolated using $F_c=0.53$, 0.60, 0.58, 0.62, and 0.65 for He, Ar, Ne, N_2, and CF_4, respectively. Collision efficiencies $\beta_c(\text{He})=0.14$, $\beta_c(\text{Ar})=0.33$, $\beta_c(\text{Ne})=0.26$, $\beta_c(N_2)=0.42$, and $\beta_c(CF_4)=0.60$ were derived from theoretical analysis of the data.

(c) CO_2 laser-induced temperature jump measurements with NO_2-N_2O_4-N_2O_3-NO-SiF_4-Ar mixtures. Temperature jumps of 0.5–3 K displace the equilibrium towards NO and NO_2. The subsequent relaxation toward equilibrium was monitored by UV absorption of N_2O_3 at 253 nm. Ar concentrations were varied from

0.5 to 200 bar. Extrapolations towards the limiting rate coefficients were made using F_c=0.6. A collisional efficiency of $\beta_c(Ar)=0.3$ was derived by theoretical analysis.

Preferred Values

$k_0=2.3\times10^{-34}$ $(T/300)^{-7.7}$ [Ar] cm^3 molecule^{-1} s^{-1} over the temperature range 208–300 K.

$k_0=3.1\times10^{-34}$ $(T/300)^{-7.7}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 208–300 K.

Reliability

$\Delta\log k_0=\pm0.3$ at 298 K.

$\Delta n=\pm1$.

Comments on Preferred Values

The preferred values for M=Ar are from Markwalder *et al.*[3] The data recommended for $M=N_2$ are from rate coefficients of Ref. 3 for M=Ar after conversion by the ratio $k_0(N_2)/k_0(Ar)=1.36$ of Smith and Yarwood.[2]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.4\pm1)\times10^{-12}$	208	Smith and Yarwood, 1987[2]	(a)
$(5.8\pm1.6)\times10^{-12}$	227	Markwalder, Gozel, and van den Bergh, 1993[3]	(b)
$(2.7\pm0.9)\times10^{-15}$ $T^{(1.4\pm0.2)}$	227–260		

Comments

(a) See comment (b) for k_0.

(b) See comment (c) for k_0.

Preferred Values

$k_\infty=7.9\times10^{-12}$ $(T/300)^{1.4}$ cm^3 molecule^{-1} s^{-1} over the temperature range 208–300 K.

Reliability

$\Delta\log k_\infty=\pm0.3$ at 298 K.

$\Delta n=\pm0.5$.

Comments on Preferred Values

The preferred values are those from Ref. 3 because larger pressure ranges were investigated. At 208 K, the k_∞ values from Refs. 2 and 3 are in reasonable agreement.

References

[1] I. W. M. Smith and G. Yarwood, Chem. Phys. Lett. **130**, 24 (1986).

[2] I. W. M. Smith and G. Yarwood, Faraday Discuss. Chem. Soc. **84**, 205 (1987).

[3] B. Markwalder, P. Gozel, and H. van den Bergh, J. Phys. Chem. **97**, 5260 (1993).

$N_2O_3 + M \rightarrow NO + NO_2 + M$

$\Delta H^\circ=40.5$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
5.0×10^{14} $T^{-(8.7\pm0.9)}$ exp(−4880/*T*) [Ar]	225–260	Markwalder, Gozel, and van den Bergh, 1993[1]	(a)

Comments

(a) CO_2 laser-induced temperature jump measurements with NO_2-N_2O_4-N_2O_3-NO-SiF_4-Ar mixtures. Temperature jumps of 0.5–3 K displace the equilibrium towards NO and NO_2. The subsequent relaxation toward equilibrium was monitored by UV absorption of N_2O_3 at 253 nm. Ar concentrations were varied from 0.5 to 200 bar. Extrapolations towards the limiting recombination rate coefficients were made using F_c=0.6. A collisional efficiency of $\beta_c(Ar)=0.3$ was derived by theoretical analysis. Dissociation rate coefficients were derived from the measured recombination rate coefficients and the equilibrium constant from

Chao *et al.*[2] of $K_c = 1.8\times 10^{29}\ T^{-1}\ \exp(-4880/T)$ molecule cm^{-3}.

Preferred Values

$k_0 = 1.6\times 10^{-14}\ [N_2]\ s^{-1}$ at 298 K.

$k_0 = 1.4\times 10^{-7}\ (T/300)^{-8.7}\ \exp(-4880/T)\ [Ar]\ s^{-1}$ over the temperature range 225–300 K.

$k_0 = 1.9\times 10^{-7}\ (T/300)^{-8.7}\ \exp(-4880/T)\ [N_2]\ s^{-1}$ over the temperature range 225–300 K.

Reliability

$\Delta \log k_0 = \pm 0.4$ at 298 K.

$\Delta n = \pm 1$.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The rate coefficients of Ref. 1 are adopted here for M = Ar. The preferred values for $M=N_2$ are obtained by converting $k_0(Ar)$ into $k_0(N_2)$ using $k_0(N_2)/k_0(Ar)-1.36$ from Smith and Yarwood[3] (see reaction $NO + NO_2 + M \rightarrow N_2O_3 + M$).

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.8\times 10^{14}\ T^{(0.4\pm 0.1)}\ \exp(-4880/T)$	225–260	Markwalder, Gozel, and van den Bergh, 1993[1]	(a)

Comments

(a) See comment (a) for k_0.

Preferred Values

$k_\infty = 3.6\times 10^{8}\ s^{-1}$ at 298 K.

$k_\infty = 4.7\times 10^{15}\ (T/300)^{0.4}\ \exp(-4880/T)\ s^{-1}$ over the temperature range 225–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred values are from Ref. 1, using the equilibrium constant of Ref. 2.

References

[1] B. Markwalder, P. Gozel, and H. van den Bergh, J. Phys. Chem. **97**, 5260 (1993).

[2] J. Chao, R. C. Wilhoit, and B. J. Zwolinski, Thermochim. Acta **10**, 359 (1974).

[3] I. W. M. Smith and G. Yarwood, Faraday Discuss. Chem. Soc. **84**, 205 (1987).

$NO + NO_3 \rightarrow 2NO_2$

$\Delta H^\circ = -97.6\ kJ\cdot mol^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 2.6\times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k = 1.8\times 10^{-11}\ \exp(110/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 220–400 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the room temperature values reported by Hammer *et al.*,[1] Sander and Kircher,[2] and Tyndall *et al.*,[3] which are in excellent agreement. The preferred temperature dependence is the average of the temperature dependences reported by Sander and Kircher[2] and by Tyndall *et al.*,[3] which are in excellent agreement. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] P. D. Hammer, E. J. Dlugokencky, and C. J. Howard, J. Phys. Chem. **90**, 2491 (1986).

[2] S. P. Sander and C. C. Kircher, Chem. Phys. Lett. **126**, 149 (1986).

[3] G. S. Tyndall, J. J. Orlando, C. A. Cantrell, R. E. Shetter, and J. Calvert, J. Phys. Chem. **95**, 4381 (1991).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO_2 + O_3 \rightarrow NO_3 + O_2$

$\Delta H° = -102.2$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 3.2 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.2 \times 10^{-13} \exp(-2450/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–360 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The preferred values are based on the data on the three temperature-dependent studies of Davis *et al.*,[1] Graham and Johnston,[2] and Huie and Herron.[3] The results of Cox and Coker[4] are in excellent agreement with this recommendation. The results of Verhees and Adema[5] show a similar temperature dependence but a higher preexponential factor. It was shown that wall reactions played an important role in this study.[5] The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[6]

References

[1] D. D. Davis, J. Prusazcyk, M. Dwyer, and P. Kim, J. Phys. Chem. **78**, 1775 (1974).

[2] R. A. Graham and H. S. Johnston, J. Chem. Phys. **60**, 4628 (1974).

[3] R. E. Huie and J. T. Herron, Chem. Phys. Lett. **27**, 411 (1974).

[4] R. A. Cox and G. B. Coker, J. Atmos. Chem. **1**, 53 (1983).

[5] P. W. C. Verhees and E. H. Adema, J. Atmos. Chem. **2**, 387 (1985).

[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$

$\Delta H° = -57.3$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.4 \pm 0.2) \times 10^{-33}$ [N$_2$]	298	Borrell, Cobos, and Luther, 1988[1]	(a)
$(2.4 \pm 0.5) \times 10^{-34}$ [He]	224	Brunning, Frost, and Smith, 1988[2]	(b)
$(1.0 \pm 0.1) \times 10^{-33}$ [N$_2$]	224		
$(1.8 \pm 0.3) \times 10^{-33}$ [CF$_4$]	224		
$(2.1 \pm 0.2) \times 10^{-12}\, T^{(-9.0 \pm 0.9)}$ [He]	255–273	Markwalder, Gozel, and van den Bergh, 1992[3]	(c)
Reviews and Evaluations			
$4.7 \times 10^{-35} \exp(860/T)$ [N$_2$]	250–350	Baulch, Drysdale, and Horne, 1973[4]	(d)

Comments

(a) Relaxation of NO_2-N_2O_4-N_2 mixtures after laser flash photolysis of N_2O_4 at 248 nm. The relaxation to equilibrium was observed by measuring the change in N_2O_4 absorption at 220 nm. Falloff curves (1–207 bar) were extrapolated with $F_c = 0.40$ and N=1.26. From a theoretical analysis in terms of the unimolecular rate theories, an average energy transferred per collision of -560 cm^{-1} was derived.

(b) Perturbation of equilibrium mixtures of N_2O_4 and NO_2 by photolysis of a fraction of the N_2O_4. The relaxation rate was monitored by IR absorption of N_2O_4 at 1565.5 cm^{-1}. Relative collisional efficiencies of β_c(He) : β_c(N$_2$): β_c(CF$_4$) = 0.2 : 1 : 1.9 were reported.

(c) Temperature jumps of the order of 1 K were induced by IR absorption of SiF_4 in equilibrium mixtures of NO_2-N_2O_4-He-SiF_4. The kinetics of the relaxation to equilibrium were followed by measuring the NO_2 and N_2O_4 concentrations by absorption spectroscopy at 420 and 250 nm, respectively. Falloff curves (0.3–200 bar) were extrapolated with F_c=0.52 and N=1.10.

(d) Based on data for the reverse reaction previous to 1970 and their tabulated equilibrium constant.[4]

Preferred Values

$k_0 = 1.4\times10^{-33}\ (T/300)^{-3.8}\ [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–500 K.

Reliability

$\Delta\log k_0 = \pm0.3$ at 298 K.

$\Delta n = \pm1$.

Comments on Preferred Values

The preferred values are from the most extensive data of Ref. 1, where a complete falloff curve was measured. Earlier less extensive measurements are in reasonable agreement with this curve, which uses F_c=0.40. The temperature dependence given is from the theoretical modeling of Ref. 1, rather than the limited experimental information of Ref. 3.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.3\pm1.0)\times10^{-13}$	298	Borrell, Cobos, and Luther, 1988[1]	(a)
$(1.7\pm0.3)\times10^{-18}\ T^{(2.3\pm0.2)}$	255–273	Markwalder, Gozel, and van den Bergh, 1992[3]	(b)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

Preferred Values

$k_\infty = 1.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–300 K.

Reliability

$\Delta\log k_\infty = \pm0.3$ over the temperature range 250–300 K.

Comments on Preferred Values

The preferred rate coefficient is the mean of the values of Borrell *et al.*[1] and Markwalder *et al.*[3] The temperature dependences of k_0 and k_∞ derived from the measurements of Ref. 3 appear unrealistic and are due to fitting of incomplete falloff curves.

Intermediate falloff range

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	P/Torr	M	Temp./K	Reference	Comments
Relative Rate Coefficients					
3.3×10^{-15}	60	Ar	258	Gozel, Calpini, and van den Bergh, 1984[5]	(a)
1.7×10^{-14}	770	Ar	258		

Comments

(a) Temperature-jump relaxation study, similar to Comment (c) for k_0.

References

[1] P. Borrell, C. J. Cobos, and K. Luther, J. Phys. Chem. **92**, 4377 (1988).

[2] J. Brunning, M. J. Frost, and I. W. M. Smith, Int. J. Chem. Kinet. **20**, 957 (1988).

[3] B. Markwalder, P. Gozel, and H. van den Bergh, J. Chem. Phys. **97**, 5472 (1992).

[4] D. L. Baulch, D. D. Drysdale, and D. G. Horne, *Evaluated Kinetic Data for High Temperature Reactions*, Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System Vol. 2 (Butterworths, London, 1973).

[5] P. Gozel, B. Calpini, and H. van den Bergh, Isr. J. Chem. **24**, 210 (1984).

$N_2O_4 + M \rightarrow NO_2 + NO_2 + M$

$\Delta H° = 57.3\ kJ \cdot mol^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comment
Absolute Rate Coefficients			
$1.29\times10^{-5}(T/300)^{-3.8}\exp(-6460/T)\ [N_2]$	300-500	Borrell, Cobos, and Luther, 1988[1]	(a)
$1.6\times10^{19}\ T^{(-10.0\pm1.0)}\exp[-(6790\pm700)/T]\ [He]$	255-273	Markwalder, Gozel, and van den Bergh, 1992[2]	(b)
Reviews and Evaluations			
$4.2\times10^{-7}\exp(-5550/T)\ [N_2]$	250-350	Baulch, Drysdale, and Horne, 1973[3]	(c)

Comments

(a) Relaxation of NO_2-N_2O_4-N_2 mixtures after laser flash photolysis of N_2O_4 at 248 nm. The relaxation to equilibrium was observed by measuring the change in N_2O_4 absorption at 220 nm. Falloff curves (1–207 bar) were extrapolated with $F_c=0.40$ and $N=1.26$. The equilibrium constant from Ref. 4 was employed.

(b) Temperature jumps of the order 1 K were induced by IR absorption of SiF_4 in equilibrium mixtures of NO_2-N_2O_4-He-SiF_4. The kinetics of the relaxation to equilibrium were followed by measuring the NO_2 and N_2O_4 concentrations by absorption spectroscopy at 420 and 250 nm, respectively. Falloff curves (0.3–200 bar) were extrapolated with $F_c=0.52$ and $N=1.10$. Equilibrium constants from Ref. 5 were employed.

(c) Based on the shock-wave studies of Refs. 6 and 7.

Preferred Values

$k_0=6.1\times10^{-15}\ [N_2]\ s^{-1}$ at 298 K.

$k_0=1.3\times10^{-5}\ (T/300)^{-3.8}\exp(-6400/T)\ [N_2]\ s^{-1}$ over the temperature range 300–500 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are from the measurements of Ref. 1 in combination with the equilibrium constants from Ref. 4. These data are based on the most complete falloff curve at 300 K, using $F_c=0.40$. The temperature dependence is from a theoretical analysis, in good agreement with the evaluation from Ref. 3.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$7.7\times10^{15}(T/300)^{-1.1}\exp(-6460/T)$	300-600	Borrell, Cobos, and Luther, 1988[1]	(a)
$2.8\times10^{13}\ T^{(1.3\pm0.2)}\exp[-(6790\pm700)/T]$	255-273	Markwalder, Gozel, and van den Bergh, 1992[2]	(b)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

Preferred Values

$k_\infty=4.4\times10^{6}\ s^{-1}$ at 298 K.

$k_\infty=1.15\times10^{16}\exp(-6460/T)\ s^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.4$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred rate coefficient at room temperature is the average of the values of Borrell *et al.*[1] and Markwalder *et al.*[2] The recommended temperature coefficient corresponds to a temperature-independent value of k_∞ for the reverse recombination.

Intermediate falloff range

Rate coefficient data

[illegible]	P/Torr	M	Temp./K	Reference	Comments
Relative Rate Coefficients					
4.1×10^{-15}	760	NO_2/N_2O_4	298	Fiedler and Hess, 1990[8]	(a)
$(4.1\pm0.8)\times10^{-15}$	2.2–6.5	NO_2/N_2O_4	298	Van Roozendael and Herman, 1990[8]	(b)

Comments

(a) Chemical relaxation of N_2O_4 was studied by Ar ion laser excited acoustic resonances of a cylindrical cavity. The reaction was investigated by measuring resonances profiles of the first radial mode. An activation energy of 36 kJ mol^{-1} was derived between 273 and 317 K. The efficiency of collision varied between 0.96 and 0.5 over the range 273–317 K.

(b) Nonresonant optoacoustic experiments in NO_2-N_2O_4 mixtures. NO_2 was monitored by IR absorption at 1601 cm^{-1}.

References

[1] P. Borrell, C. J. Cobos, and K. Luther, J. Phys. Chem. **92**, 4377 (1988).

[2] B. Markwalder, P. Gozel, and H. van den Bergh, J. Chem. Phys. **97**, 5472 (1992).

[3] D. L. Baulch, D.D. Drysdale, and D. G. Horne, *Evaluated Kinetic Data for High Temperature Reactions*, Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System Vol. 2 (Butterworths, London, 1973).

[4] J. Chao, R. C. Wilhoit, and B. J. Zwolinski, Thermochim. Acta **10**, 359 (1974).

[5] A. J. Vosper, J. Chem. Soc. **A1**, 625 (1970).

[6] T. Carrington and N. Davidson, J. Phys. Chem. **57**, 418 (1953).

[7] E. Zimet, J. Chem. Phys. **53**, 315 (1970).

[8] M. Fiedler and P. Hess, J. Chem. Phys. **93**, 8693 (1990).

[9] M. Van Roozendael and M. Herman, Chem. Phys. Lett. **166**, 233 (1990).

$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

$\Delta H^\circ = -95.6$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 2.7\times10^{-30}\ (T/300)^{-3.4}\ [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta\log k_0 = \pm0.10$ at 298 K.

$\Delta n = \pm0.5$.

Comments on Preferred Values

The results of Orlando *et al.*[1] are in excellent agreement with our previous recommended values,[2] which are also adopted here.

High-pressure rate coefficients

Preferred Values

$k_\infty = 2.0\times10^{-12}\ (T/300)^{0.2}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–500 K.

Reliability

$\Delta\log k_\infty = \pm0.2$ at 298 K.

$\Delta n = \pm0.6$.

Comments on Preferred Values

Very good agreement between the rate coefficients reported by Orlando *et al.*[1] and our previously recommended-values[2] are observed. The preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] J. J. Orlando, G. S. Tyndall, C. A. Cantrell, and J. G. Calvert, J. Chem. Soc. Faraday Trans. **87**, 2345 (1991).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$

$\Delta H° = 95.6\ kJ \cdot mol^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.04\times10^{-3}\ (T/300)^{-3.5}\exp(-11000/T)\ [N_2]$	253–384	Cantrell *et al.*, 1993[1]	(a)
Reviews and Evaluations			
$2.2\times10^{-3}(T/300)^{-4.4}\exp(-11080/T)\ [N_2]$	220–300	IUPAC, 1992[2]	(b)
$8.2\times10^{-4}(T/300)^{-3.9}\exp(-11000/T)$ [air]	200–300	NASA, 1994[3]	(c)

Comments

(a) Thermal decomposition of N_2O_5 in the presence of NO in N_2. FTIR analysis of N_2O_5 in a stainless steel cell equipped with multiple path optics. Falloff curves over the gas density 4.3×10^{14} to 1.1×10^{20} molecule cm^{-3} were analyzed using $F_c=[2.5\exp(-1950/T)+0.9\exp(-T/430)]$. In the analysis, data from Refs. 4 and 5 were also taken in account.

(b) Based on the recommendation of a previous evaluation.[6]

(c) Rate coefficients evaluated from the recommended rate coefficients for the reverse reaction and the equilibrium constant.

Preferred Values

$k_0=9.5\times10^{-20}\ [N_2]\ s^{-1}$ at 298 K.

$k_0=1.0\times10^{-3}\ (T/300)^{-3.5}\exp(-11000/T)\ [N_2]\ s^{-1}$ over the temperature range 200–400 K.

Reliability

$\Delta\log k_0=\pm0.2$ at 298 K

$\Delta n=\pm0.5$.

Comments on Preferred Values

The recommended values of the previous evaluation[2] have been slightly modified according to the recent study of Cantrell *et al.*[1] In this way both the preferred values of the recombination and dissociation low-pressure rate coefficients and the recommended values for the recombination and dissociation high-pressure rate coefficients are internally consistent through the same equilibrium constant. The equilibrium constant at room temperature of $2.3\times10^{-11}\ cm^3\ molecule^{-1}$ compares well with other recently reported values.[7,8]

High-pressure rate coefficients

Rate coefficient data

$k_\infty/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.22\times10^{14}\ (T/300)^{-0.2}\exp(-11000/T)$	253–384	Cantrell *et al.*, 1993[1]	(a)
Reviews and Evaluations			
$9.7\times10^{14}(T/300)^{0.1}\exp(-11080/T)$	200–300	IUPAC, 1992[2]	(b)
$5.5\times10^{14}\ (T/300)^{-0.7}\exp(-11000/T)$	200–300	NASA, 1994[3]	(c)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

(c) See comment (c) for k_0.

Preferred Values

$k_\infty=6.9\times10^{-2}\ s^{-1}$ at 298 K.

$k_\infty=9.7\times10^{14}\ (T/300)^{0.1}\exp(-11080/T)\ s^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta\log k_\infty=\pm0.3$ at 298 K.

$\Delta n=\pm0.2$.

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992,[2] and agree well with the recent determination.[1] For the equilibrium constant, see comments on preferred values for k_0.

References

[1] A. Cantrell, R. E. Shetter, J. G. Calvert, G. S. Tyndall, and J. J. Orlando, J. Phys. Chem. **97**, 9141 (1993).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] P. Connell and H. S. Johnston, Geophys. Res. Lett. **6**, 553 (1979).
[5] A. A. Viggiano, J. A. Davidson, F. C. Fehsenfeld, and E. E. Ferguson, J. Chem. Phys. **74**, 6113 (1981).
[6] CODATA, Supplement I, 1982 (see references in Introduction).
[7] J. Hjorth, J. Notholt, and G. Restelli, Int. J. Chem. Kinet. **24**, 51 (1992).
[8] H. O. Pritchard, Int. J. Chem. Kinet. **26**, 61 (1994).

$N_2O_5 + H_2O \rightarrow 2HNO_3$

$\Delta H^\circ = -39.6$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k < 2 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This upper limit is based on the data of Tuazon *et al.*,[1] Atkinson *et al.*,[2] Hjorth *et al.*,[3] and Hatakeyama and Leu.[4] It is possible that the observed decays proceed only by heterogeneous processes. While the lower value of Sverdrup *et al.*[5] may in fact be closer to the value of the rate coefficient for the homogeneous gas phase reaction, because it is less direct we prefer the more conservative recommendation given here. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.[6]

References

[1] E. C. Tuazon, R. Atkinson, C. N. Plum, A. M. Winer, and J. N. Pitts, Jr., Geophys. Res. Lett. **10**, 953 (1983).
[2] R. Atkinson, E. C. Tuazon, H. Mac Leod, S. M. Aschmann, and A. M. Winer, Geophys. Res. Lett. **13**, 117 (1986).
[3] J. Hjorth, G. Ottobrini, F. Cappellani, and G. Restelli, J. Phys. Chem. **91**, 1565 (1987).
[4] S. Hatakeyama and M.-T. Leu, J. Phys. Chem. **93**, 5784 (1989).
[5] G. M. Sverdrup, C. W. Spicer, and G. F. Ward, Int. J. Chem. Kinet. **19**, 191 (1987).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

HONO + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
HONO + $h\nu \rightarrow$ HO + NO	(1)	209	572
$\rightarrow$ H + NO_2	(2)	331	361
$\rightarrow$ HNO + O(^{3}P)	(3)	428	280

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(H)$	355	Burkholder *et al.*, 1992[1]	(a)

Comments

(a) Relative yield of H atoms inferred from secondary HO production observed in the laser photolysis of HONO at 355 nm. HO radicals were produced via the reaction: H + $NO_2 \rightarrow$ HO + NO, involving impurity NO_2. The data obtained were consistent with $\phi_2 = 0.1$ at 355 nm.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\sigma/\mathrm{cm}^2$
190	127	260	8.0	330	10.9
195	172	265	5.2	335	7.7
200	197	270	3.4	340	19.7
205	220	275	2.5	345	11.2
210	214	280	-	350	13.4
215	179	285	-	355	27.6
220	146	290	-	360	9.4
225	120	295	-	365	18.8
230	86	300	0.0	370	24.0
235	60	305	0.8	375	5.7
240	42	310	1.9	380	10.8
245	30	315	2.9	385	16.9
250	18.5	320	5.2	390	2.8
255	12.4	325	5.8	395	0.7

Quantum Yields

$\phi_1+\phi_2+\phi_3=1.0$ throughout this wavelength range.
$\phi_1=1.0$ at $\lambda>366$ nm, decreasing to 0.4 at $\lambda=310$ nm.
$\phi_2=0.0$ at $\lambda>366$ nm, increasing to 0.6 at $\lambda=310$ nm.

Comments on Preferred Values

The preferred values for the cross-sections in the 300–395 nm range, which are unchanged from our previous IUPAC evaluation,[2] are obtained from the data of Bongartz *et al.*[3] by averaging their 0.5 nm intervals centered on the wavelengths specified in the table.

The laser photolysis experiments of Burkholder *et al.*[1] in the first absorption band at 355 nm show strong indirect evidence for the production of H atoms in HONO photolysis at wavelengths below the threshold for reaction (2), as originally proposed by Cox.[4] Further evidence for an increasing contribution from reaction (2) with decreasing wavelength in the first absorption band comes from a comparison of the relative absorption spectra determined by conventional light absorption methods and by laser photofragment spectroscopy of the HO radical product from channel (1). When the spectra are normalized to peaks at $\lambda>370$ nm, the cross-section values of Vasudev[5] at $\lambda<350$ nm obtained from the HO radical yield are consistently smaller than those measured in absorption by Bongartz *et al.*[3] The difference increases approximately linearly to approximately 60% at 310 nm. This difference could be attributed to a decrease in ϕ(HO) from unity at 366 nm to 0.4 at 310 nm. The balance could be attributed to H atom production, ϕ_2, with $\phi_1+\phi_2=1.0$ in the first absorption band.

In the second absorption band, cross-sections over the range 185–275 nm are based on the data of Kenner *et al.*,[6] which also show that reaction (1) is the main photodissociation channel in this region. However, in view of the clear indication of H atom production in the first absorption band a contribution from reaction (2) at shorter wavelengths seems likely.

References

[1] J. B. Burkholder, A. Mellouki, R. Talukdar, and A. R. Ravishankara, Int. J. Chem. Kinet. **24**, 711 (1992).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] A. Bongartz, J. Kames, F. Welter, and U. Schurath, J. Phys. Chem. **95**, 1076 (1991).
[4] R. A. Cox, J. Photochem. **3**, 175 (1974).
[5] R. Vasudev, Geophys. Res. Lett. **17**, 2153 (1990).
[6] R. D. Kenner, F. Rohrer, and F. Stuhl, J. Phys. Chem. **90**, 2635 (1986).

$HONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°/\mathrm{kJ \cdot mol^{-1}}$	$\lambda_{\mathrm{threshold}}/\mathrm{nm}$
$HONO_2 + h\nu \rightarrow HO + NO_2$	(1)	200	598
$\rightarrow HONO + O(^3P)$	(2)	298	401
$\rightarrow H + NO_3$	(3)	418	286
$\rightarrow HONO + O(^1D)$	(4)	488	245
$\rightarrow HO + NO + O(^3P)$	(5)	499	239

Absorption cross-section data

Wavelength range/nm	References	Comments
195–350	Burkholder *et al.*, 1993[1]	(a)

Comments

The temperature dependence of HNO_3 absorption cross-sections were measured using a diode array spectrometer with a resolution of <0.4 nm between 240–360 K. Absorption cross-sections were determined using both absolute pressure measurements at 298 K and a dual cell arrangement to measure absorption at various temperatures relative to 298 K. A review of all previous experimental values was given together with an assessment of temperature-dependence effects on the stratospheric photolysis rates of HNO_3.

Quantum yield data

Measurement	Wavelength/nm	Reference	Comment
ϕ[HO], ϕ[O(^{3}P)], ϕ[O(^{1}D)], ϕ [H(^{2}S)]	248, 222, 193	Turnipseed *et al.*, 1992[2]	(b)
ϕ[HO]	248, 193	Schiffman, Nelson, and Nesbitt, 1993[3]	(c)
ϕ(1), ϕ(4), ϕ(5)	193	Felder, Yang, and Huber, 1993[4]	(d)

Comments

(a) Quantum yields for HO radicals, O[(^{3}P)+(^{1}D)] atoms, O(^{1}D) atoms and H atoms were measured in pulsed laser photolysis systems at 248, 222, and 193 nm, using LIF detection for HO($X^2\Pi$) radicals and atomic resonance fluorescence for O(^{3}P) and H(^{2}S) atoms. ϕ [HO] was measured relative to the yield of HO radicals from H_2O_2 photolysis (ϕ [HO]=2.0 at 248 nm[4] and ϕ [HO]=1.5 at 193 nm[5]). ϕ [O{(^{3}P)+(^{1}D)}] was measured relative to the O atom yield from ozone photolysis at 248 nm (ϕ=1) and 193 nm (ϕ=1.2).[6] ϕ [H (^{2}S)] was measured relative to the H atom yield from the photolysis of O_3/H_2 mixtures where the H atoms are produced in the O(^{1}D) + H_2 reaction. Measurements gave: ϕ [HO]=0.95±0.09 at 248 nm, 0.90 ±0.11 at 222 nm, and 0.33±0.06 at 193 nm. ϕ [O{(^{3}P)+(^{1}D)}] was observed to be 0.031±0.010, 0.20±0.03, 0.81±0.13 at 248, 222, and 193 nm respectively, with exclusively O(^{3}P) production at 248 nm. ϕ [O(^{1}D)] was 0.074±0.03 at 222 nm and 0.28±0.13 at 193 nm. H atom yields were very low; only at 193 nm were any H atoms detected with ϕ [H(^{2}S)] <0.012.

(b) Absolute quantum yields were measured for HO radical production from 248 nm and 193 nm pulsed laser photolysis of HNO_3 and H_2O_2 in a flow tube. HO radicals were detected by tunable diode laser absorption. ϕ [HO] was measured to be 0.47±0.06 and 0.75±0.10 at 193 and 248 nm, respectively. Equivalent values for HO radical yields from H_2O_2 photolysis were ϕ=1.22±0.13 and ϕ=1.58±0.23, respectively.

(c) Photofragment translation spectroscopy investigation of $HONO_2$ photolysis at 193 nm. The primary processes and their relative yields were deduced from photofragment time-of-flight signals at masses 16 (O^+), 17 (OH^+), 30 (NO^+), and 46 (NO_2^+). Relative yields for reactions (1) and (4) of 0.6±0.1 and 0.4 ±0.1, respectively, were obtained. Hot NO_2 photofragments were produced in reaction (1) in the ratio 2:1, relative to stable NO_2, leading to production of O(^{3}P) atoms via reaction channel (5).

Preferred Values

Absorption cross-sections at 298 K[a]

λ/nm	$10^{20}\sigma$/cm^2	10^3 B/K^{-1}	λ/nm	$10^{20}\sigma$/cm^2	10^3 B/K^{-1}
190	1360	0	270	1.62	1.45
195	1016	0	275	1.38	1.60
200	588	1.66	280	1.12	1.78
205	280	1.75	285	0.858	1.99
210	104	1.97	290	0.615	2.27
215	36.5	2.17	295	0.412	2.61
220	14.9	2.15	300	0.263	3.10
225	8.81	1.90	305	0.150	3.64
230	5.75	1.80	310	0.081	4.23
235	3.75	1.93	315	0.041	5.20
240	2.58	1.97	320	0.020	6.45
245	2.11	1.68	325	0.0095	7.35
250	1.97	1.34	330	0.0043	9.75
255	1.95	1.16	335	0.0022	10.1
260	1.91	1.14	340	0.0010	11.8
265	1.80	1.20	345	0.0006	11.2
			350	0.0004	9.30

[a] Temperature dependence given by the expression: $\log_e\sigma=\log_e\sigma(298)+B(T-298)$ with T in K.

Quantum yields

	λ/nm		
	⩾248	222	193
$\phi(1)+\phi(5)$	>0.97	0.90±0.10	0.60±0.20
$\phi(2)$	0.03±0.03		
$\phi(3)$	<0.01	<0.01	0.01
$\phi(4)$		0.10±0.10	0.39±0.20
$\phi(5)$		0.13±0.03	0.40±0.20

Comments on Preferred Values

The new results of Burkholder *et al.*[1] for the cross-section provide a high quality and comprehensive data set over the range of temperatures and wavelengths of significance for the atmospheric photolysis of HNO_3. Over the wavelength range 205–310 nm there is good agreement with the earlier studies of Rattigan *et al.*,[5] Biaume,[6] Molina and Molina,[7] and Johnston and Graham.[8] At $\lambda<205$ nm, the data from different studies show small but unexplained discrepancies. At $\lambda>310$ nm the room temperature results[1] are increasingly higher than all previously reported data except that of Rattigan *et al.*,[5] which is in good agreement. Values recommended previously by NASA[9] and IUPAC[10] on the basis of earlier data are therefore too low. The preferred values are those given by Burkholder *et al.*[1]

The temperature dependence reported by Burkholder *et al.*[1] is weaker than that reported previously by Rattigan *et al.*[5] However, if the data at the lowest temperature (239 K) from Ref. 5 is omitted the agreement is good, and Burkholder *et al.*[1] give values for the temperature coefficient, B, based on the two data sets[1,5] (excluding the 239 K data from Ref. 5), and these are adopted here.

The new data for the quantum yield confirm that, although reaction (1) is the dominant channel at $\lambda\geqslant260$ nm with $\phi(1)$ close to unity, other channels become important at shorter wavelengths as suggested by the earlier work of Kenner *et al.*[11] The results of Turnipseed *et al.*[2] and Schiffman *et al.*[3] are in excellent agreement at 248 nm when the relative measurements of Turnipseed *et al.*[2] are normalized to the same value of the quantum yield for HO radical production from H_2O_2. The agreement is less good at 193 nm, where the direct measurements of Schiffman *et al.*[3] give an HO radical yield higher by about 50%. The value of $\phi(H_2O_2)$ obtained by Schiffman *et al.*[3] is about 25% lower at both 248 and 193 nm than the values obtained by Vaghjiani *et al.*[12] (2.0 at 248 nm and 1.5 at 193 nm) which are recommended in the present evaluation.

The preferred values of the quantum yields $\phi(1)+\phi(5)$ [HO production] are based on the indirect studies of Johnston *et al.*[13] and the direct observations of Jolly *et al.*[14] at 222 nm, Turnipseed *et al.*,[2] and Felder *et al.*[4] The data of Schiffman *et al.*[3] are not used in view of the inconsistency of their absolute $\phi(HO)$ values for H_2O_2 dissociation. At 193 nm, O-atom production becomes a major channel but HO and O production is not mutually exclusive since reaction (5) can occur at $\lambda\leqslant239$ nm, either through excited NO_2^* or HONO*. Felder *et al.*[4] show that $\phi(5)=0.4$ at 193 nm. Ground state HONO is the likely co-product of $O(^1D)$ atoms and hence the data of Turnipseed *et al.*[2] imply $\phi(4)=0.28$ at 193 nm and 0.074 at 222 nm, which is consistent within the experimental uncertainty with the results of Felder *et al.*[4] In the absence of direct measurements of HONO at longer wavelengths, $\phi(2)$ cannot be determined; this channel is probably responsible for the small amount of O-atom production at $\lambda\geqslant239$ nm, as measured, for example, by Margitan and Watson[15] with $\phi\ [O(^3P)]=0.03$ at 266 nm. The data of Turnipseed *et al.*[2] show that H atom production, and hence $\phi(3)$, is significant only at 193 nm with $\phi(3)=<0.012$.

References

[1] J. B. Burkholder, R. K. Talukdar, A. R. Ravishankara, and S. Solomon, J. Geophys. Res. **98**, 22937 (1993).

[2] A. A. Turnipseed, G. L. Vaghjiani, J. E. Thompson, and A. R. Ravishankara, J. Chem. Phys. **96**, 5887 (1992).

[3] A. Schiffman, D. D. Nelson, Jr., and D. J. Nesbitt, J. Chem. Phys. **98**, 6935 (1993).

[4] P. Felder, X. Yang, and J. R. Huber, Chem. Phys. Lett. **215**, 221 (1993).

[5] O. Rattigan, E. Lutman, R. L. Jones, R. A. Cox, K. Clemitshaw, and J. Williams, J. Photochem. Photobiol. A: Chem. **66**, 313 (1992); Corrigendum, *ibid.* **69**, 125 (1992).

[6] F. Biaume, J. Photochem. **2**, 139 (1973).

[7] L. T. Molina and M. J. Molina, J. Photochem. **15**, 97 (1981).

[8] H. Johnston and R. Graham, J. Phys. Chem. **77**, 62 (1973).

[9] NASA Evaluation No. 9, 1990 (see references in Introduction).

[10] IUPAC, Supplement III, 1989 (see references in Introduction).

[11] R. D. Kenner, F. Rohrer, Th. Papenbrock, and F. Stuhl, J. Phys. Chem. **90**, 1294 (1986).

[12] G. L. Vaghjiani, A. A. Turnipseed, R. F. Warren, and A. R. Ravishankara, J. Chem. Phys. **96**, 5878 (1992).

[13] H. S. Johnston, S.-G. Chang, and G. Whitten, J. Phys. Chem. **78**, 1 (1974).

[14] G. S. Jolly, D. L. Singleton, D. J. McKenney, and G. Paraskevopoulos, J. Chem. Phys. **84**, 6662 (1986).

[15] J. J. Margitan and R. T. Watson, J. Phys. Chem. **86**, 3819 (1982).

$HO_2NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2$ (1)	105	1141
$\rightarrow HO + NO_3$ (2)	170	704

Preferred Values

Absorption cross-sections at 296 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
190	1010	260	28.4
195	816	265	22.9
200	563	270	18.0
205	367	275	13.3
210	239	280	9.3
215	161	285	6.2
220	118	290	3.9
225	93.2	295	2.4
230	78.8	300	1.4
235	68.0	305	0.85
240	57.9	310	0.53
245	49.7	315	0.39
250	41.1	320	0.24
255	34.9	325	0.15
		330	0.09

Quantum Yields

$\phi_1 = 0.61$.
$\phi_2 = 0.39$.

Comments on Preferred Values

The preferred absorption cross-section values are based on the data of Singer *et al.*[1] and Molina and Molina,[2] which are in excellent agreement at wavelengths between 210–300 nm. Between 300 and 320 nm the cross-sections of Singer *et al.*[1] are approximately a factor of 2 lower. A simple mean of the two data sets is taken over the whole range.

For the quantum yield we recommend values based on the measurements of Mac Leod *et al.*,[3] with a small upward revision to take into account the present recommendation for the absorption cross-section for H_2O_2. The uncertainties on the quantum yields are large and it should be noted that they are based on data at a single wavelength. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] R. J. Singer, J. N. Crowley, J. P. Burrows, W. Schneider, and G. K. Moortgat, J. Photochem. Photobiol. **48**, 17 (1989).
[2] L. T. Molina and M. J. Molina, J. Photochem. **15**, 97 (1981).
[3] H. Mac Leod, G. P. Smith, and D. M. Golden, J. Geophys. Res. **93**, 3813 (1988).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$NO_2 + h\nu \rightarrow NO + O(^3P)$ (1)	300	398
$\rightarrow NO + O(^1D)$ (2)	490	244

Absorption cross-section data

Wavelength range/nm	Reference	Comments
440–460	Amoruso *et al.*, 1993[1]	(a)
310–570	Harwood and Jones, 1994[2]	(b)

Comments

(a) Measurements of the NO_2 absorption cross-section in a limited wavelength range, with estimates of the NO_2-N_2O_4 equilibrium constant.

(b) Cross-sections measured over the temperature range of 213–298 K and with NO_2 concentrations of $(1.5–20.0) \times 10^{15}$ molecule cm^{-3} using a diode array spectrometer. Absorption due to N_2O_4 was corrected for using data for the cross-sections for N_2O_4 and K_p for dimerization of NO_2 determined simultaneously in the same experiments. The spectral resolution was 0.54 nm FWHM. Averaged cross-sections over 5 nm intervals were given as well as high-resolution data.

Preferred Values

Absorption cross-sections[a]

λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$
190		315	21.53	440	45.52
195		320	24.77	445	46.58
200		325	28.07	450	47.58
205	43.06	330	31.33	455	40.02
210	47.20	335	34.25	460	41.85
215	49.54	340	37.98	465	39.65
220	45.61	345	40.65	470	32.38
225	37.88	350	43.13	475	36.78
230	27.39	355	47.17	480	31.97
235	16.69	360	48.33	485	24.19
240	9.31	365	51.66	490	28.95
245	4.74	370	53.15	495	27.09
250	2.48	375	55.08	500	17.22
255	1.95	380	56.44	505	22.48
260	2.24	385	57.57	510	21.61
265	2.73	390	59.27	515	14.95
270	4.11	395	58.45	520	15.00
275	4.90	400	60.21	525	16.58
280	5.92	405	57.81	530	14.18
285	7.39	410	59.99	535	9.88
290	9.00	415	56.51	540	10.10
295	10.91	420	58.12	545	11.83
300	13.07	425	53.81	550	10.17
305	15.73	430	50.81	555	7.34
310	18.61	435	51.70	560	5.62
				565	7.87

[a] Absorption cross-sections in the range 190–565 nm, averaged over 5 nm intervals, are independent of temperature.

Quantum Yields

λ/nm	ϕ	λ/nm	ϕ	λ/nm	ϕ
<310	1.00	370	0.98	406	0.2
315	0.99	375	0.98	408	0.1
320	0.99	380	0.97	410	0.1
325	0.99	385	0.97	412	0.0
330	0.99	390	0.96	414	0.0
335	0.99	392	0.96	416	0.0
340	0.99	394	0.95	418	0.0
345	0.99	396	0.92	420	0.0
350	0.99	398	0.82	422	0.01
355	0.99	400	0.82	424	0.00
360	0.98	402	0.69		
365	0.98	404	0.42		

Comments on Preferred Values

The new absorption cross-sections of Harwood and Jones are in very good agreement with the earlier data of Davidson *et al.*,[3] Bass *et al.*,[4] and Schneider *et al.*[5] at room temperature. The agreement in the 5 nm-averaged cross-sections for the range 320–435 nm is within ±4% of the data of Davidson *et al.*,[3] which were recommended previously.

No significant temperature dependence of the 0.5 nm-averaged cross-sections was observed in the wavelength region 320–535 nm (Davidson *et al.*[3] observed a very weak temperature dependence, in contrast to earlier studies which showed a larger effect). The new measurements support the suggestion of Davidson *et al.*[3] that the discrepancies observed by Bass *et al.*,[4] Davenport *et al.*,[6] and Hicks *et al.*[7] can be accounted for by incorrect compensation for N_2O_4. Roscoe and Hind[8] have reached similar conclusions in their recent critical review of the implications of the $NO_2 \rightleftarrows N_2O_4$ equilibrium for earlier determinations of NO_2 absorption crosssections and their temperature dependence.

Cross-sections measured by Harwood and Jones[2] at higher resolution showed a sharpening of the spectral features of the NO_2 spectrum as the temperature was decreased, but no shift in wavelength was observed. The apparent shifts in wavelength with temperature observed in certain regions by Davidson *et al.*[3] and Schneider *et al.*[5] were probably due to calibration errors.

The preferred values for the cross-sections at 298 K, averaged over 5 nm intervals for the range 270–410 nm, are mean values from the data of Harwood and Jones[2] and Davidson *et al.*[3] and are virtually unchanged from the previously recommended values for 273 K. The averaged values in the range 410–565 nm (not previously given in the IUPAC evaluations) are taken from Harwood and Jones.[2] The preferred values for the wavelength range 185–265 nm, also averaged over 5 nm wavelength intervals, are taken from Table 4 of Schneider *et al.*[5] The averaged values are independent of temperature over the whole range.

The preferred quantum yields are those recommended by Gardner *et al.*[9] (see previous IUPAC evaluation[10]). They are based on a best fit to the data of Gardner *et al.*[9] from 334–404 nm, Jones and Bayes[11] for 297–412 nm, Davenport[6] for [illegible]–420 nm, and Harker *et al.*[12] (corrected for cross-sections) for 397–420 nm. The results of Gardner *et al.*[9] support the results of Jones and Bayes[11] showing that the primary quantum yield is nearly unity throughout the entire wavelength region from 290–390 nm, and that the low values reported by Harker *et al.*[12] for the 375–396 nm region must be in error. Possible reasons for these low values are discussed in Ref. 9.

References

[1] A. Amoruso, L. Crescentini, G. Fiocco, and M. Volpe, J. Geophys. Res. **98**, 16857 (1993).

[2] M. H. Harwood and R. L. Jones, J. Geophys. Res. **99**, 22955 (1994).

[3] J. A. Davidson, C. A. Cantrell, A. H. McDaniel, R. E. Shetter, S. Madronich, and J. G. Calvert, J. Geophys. Res. **93**, 7105 (1988).

[4] A. M. Bass, A. E. Ledford, Jr., and A. H. Laufer, J. Res. Natl. Bur. Stand. Sect. A, **80**, 143 (1976).

[5] W. Schneider, G. K. Moortgat, G. S. Tyndall, and J. P. Burrows, J. Photochem. Photobiol. A: Chem. **40**, 195 (1987).

[6] J. E. Davenport, "*Determination of NO_2 photolysis parameters for stratospheric modeling*," Final Report FAA-EQ-78-14, FAA Washington, D.C., 1978.

[7] E. Hicks, B. Leroy, P. Rigaud, J. Jourdain, and G. Le Bras, J. Chim. Phys. **76**, 693 (1979).

[8] H. K. Roscoe and A. K. Hind, J. Atmos. Chem. **16**, 257 (1993).

[9] E. P. Gardner, P. D. Sperry, and J. G. Calvert, J. Geophys. Res. **92**, 6642 (1987).

[10] IUPAC, Supplement III, 1989 (see references in Introduction).

[11] I. T. N. Jones and K. D. Bayes, J. Chem. Phys. **59**, 4836 (1973).

[12] A. B. Harker, W. Ho, and J. J. Ratto, Chem. Phys. Lett. **50**, 394 (1977).

$NO_3 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$NO_3 + h\nu \rightarrow NO + O_2(^3\Sigma)$	(1)	10.9	11000
$\rightarrow NO + O_2(^1\Delta)$	(2)	105.2	1137
$\rightarrow NO + O_2(^1\Sigma)$	(3)	167.8	712
$\rightarrow NO_2 + O(^3P)$	(4)	203.9	587

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\phi(NO+O_2)$, $\phi(4)$	532–662	Davis *et al.*, 1993[1]	(a)
$\phi(NO+O_2)$, $\phi(4)$	570–635	Orlando *et al.*, 1993[2]	(b)

Comments

(a) The photodissociation of NO_3 was studied using molecular beam photofragment translational spectroscopy. For internally cold NO_3, $\phi(NO + O_2) = (0.70 \pm 0.10)$ at 588 nm falling off rapidly at $\lambda \leq 587$ nm to reach <0.01 at 583 nm. $\phi(4)$ increased from 0.3 to >0.99 over this range of wavelength. Both channels appear to result from dissociation from the same vibrationally excited ground state, excited by crossing from the NO_3 $(^2E')$ state formed on excitation. The dissociation energy $D_0(O\text{–}NO_2)$ was measured as 203.7 ± 1.0 kJ mol^{-1} and corresponding values of $\Delta H_f^{\circ}(NO_3) = 78.95 \pm 1.38$ and 73.72 ± 1.38 kJ mol^{-1} at 0 K and 298 K, respectively, were determined.

(b) The photodissociation of NO_3 was studied at 298 K using pulsed laser photolysis, with resonance fluorescence detection of $O(^3P)$ atoms and $NO(X^2\Pi)$. $\phi\,[O(^3P)]$ was 1.0 from 570–585 nm, decreasing to a value <0.1 at 635 nm. $\phi(NO)$ was <0.1 at 580 nm and about 0.20 ± 0.10 at 590 nm. These data were combined with earlier results of Magnotta and Johnston[6] to provide quantum yields $\phi(NO + O_2)$ and $\phi(4)$ as a function of wavelength (586–639 nm) and to calculate photolysis rates for overhead sun at the earth's surface, with $J(NO_2 + O) = 0.19$ s^{-1}; $J(NO + O_2) = 0.016$ s^{-1}.

Preferred Values

Absorption cross-sections at 298 K and 230 K

λ/nm	$10^{19}\sigma/\mathrm{cm}^2$ 298 K	$10^{19}\sigma/\mathrm{cm}^2$ 230 K	λ/nm	$10^{19}\sigma/\mathrm{cm}^2$ 298 K	$10^{19}\sigma/\mathrm{cm}^2$ 230 K	λ/nm	$10^{19}\sigma/\mathrm{cm}^2$ 298 K	$10^{19}\sigma/\mathrm{cm}^2$ 230 K
400	0.0	0.4	500	11.3	11.5	600	27.6	27.8
401	0.0	0.5	501	11.1	10.7	601	28.6	28.5
402	0.0	0.5	502	11.1	10.4	602	33.2	33.4
403	0.2	0.5	503	11.1	11.1	603	38.0	40.3
404	0.0	0.3	504	12.6	12.5	604	43.7	48.1
405	0.3	0.7	505	12.8	13.1	605	43.6	49.8
406	0.2	0.6	506	13.4	14.1	606	33.2	37.1
407	0.1	0.5	507	12.8	13.1	607	24.0	24.8
408	0.3	0.5	508	12.7	12.2	608	18.5	17.9
409	0.0	0.7	509	13.5	13.2	609	17.1	16.6
410	0.1	0.5	510	15.1	15.5	610	17.7	17.3
411	0.2	0.7	511	17.3	18.7	611	19.1	19.4
412	0.5	0.4	512	17.7	19.8	612	22.3	23.6
413	0.5	0.7	513	16.0	18.0	613	26.3	30.0
414	0.2	1.1	514	15.8	16.2	614	25.5	28.6
415	0.6	0.7	515	15.8	15.9	615	22.6	24.2
416	0.6	0.7	516	15.6	16.4	616	20.9	21.1
417	0.7	1.0	517	14.9	14.4	617	21.1	20.6
418	0.5	1.0	518	14.4	14.0	618	23.9	22.9
419	0.8	1.0	519	15.4	14.9	619	25.6	25.4
420	0.8	1.3	520	16.8	16.2	620	32.7	33.5
421	0.8	1.2	521	18.3	17.7	621	52.4	58.9
422	0.9	1.2	522	19.3	19.3	622	101.8	113.6
423	1.1	1.2	523	17.7	17.9	623	147.3	163.5
424	0.9	1.3	524	16.4	15.7	624	120.5	129.9
425	0.7	1.6	525	15.8	15.0	625	83.8	94.3
426	1.4	1.5	526	16.3	15.7	626	73.0	82.6
427	1.4	1.2	527	18.1	18.1	627	75.3	90.0
428	1.2	1.5	528	21.0	22.3	628	73.7	88.3
429	1.1	1.3	529	23.9	25.6	629	69.8	84.6
430	1.7	1.6	530	22.3	23.1	630	67.6	84.0
431	1.3	1.7	531	20.9	21.3	631	48.4	57.1
432	1.5	1.7	532	20.2	20.6	632	32.7	37.3
433	1.8	1.9	533	19.5	19.8	633	21.7	23.5
434	1.8	2.1	534	20.4	21.3	634	16.4	16.2
435	1.6	2.2	535	23.0	24.9	635	14.4	13.1
436	1.5	2.2	536	25.7	28.7	636	16.9	15.2
437	1.8	1.9	537	25.8	28.6	637	20.7	18.8
438	2.1	2.1	538	23.4	24.4	638	20.3	17.7
439	2.0	2.6	539	20.4	21.0	639	15.8	13.3
440	1.9	2.2	540	21.0	21.2	640	12.3	10.6
441	1.8	2.3	541	20.4	20.4	641	10.0	8.9
442	2.1	2.2	542	18.8	18.5	642	9.2	7.9
443	1.8	2.2	543	16.8	16.4	643	9.7	7.6
444	1.9	2.2	544	17.0	16.2	644	9.5	7.9
445	2.0	2.7	545	19.6	20.0	645	8.6	7.5
446	2.4	2.7	546	24.2	24.8	646	7.5	6.5
447	2.9	3.1	547	29.1	30.9	647	7.0	6.4
448	2.4	3.4	548	29.8	31.3	648	6.2	5.9
449	2.8	3.1	549	27.1	27.8	649	5.4	5.0
450	2.9	3.1	550	24.8	26.0	650	5.0	4.7
451	3.0	3.5	551	24.3	25.9	651	5.5	5.2
452	3.3	3.7	552	24.7	26.7	652	6.1	6.2
453	3.1	3.5	553	25.3	27.5	653	7.1	7.4
454	3.6	3.7	554	27.8	31.0	654	8.2	8.6
455	3.6	3.8	555	31.1	35.6	655	9.8	10.3
456	3.6	3.4	556	32.6	36.7	656	13.3	13.5
457	4.0	3.9	557	32.9	36.8	657	17.1	17.3
458	3.7	4.4	558	35.1	39.5	658	24.2	24.3

Absorption cross-sections at 298 K and 230 K—Continued

λ/nm	$10^{19}\sigma/\mathrm{cm}^2$ 298 K	$10^{19}\sigma/\mathrm{cm}^2$ 230 K	λ/nm	$10^{19}\sigma/\mathrm{cm}^2$ 298 K	$10^{19}\sigma/\mathrm{cm}^2$ 230 K	λ/nm	$10^{19}\sigma/\mathrm{cm}^2$ 298 K	$10^{19}\sigma/\mathrm{cm}^2$ 230 K
459	4.2	4.2	559	37.2	42.4	659	40.7	40.0
460	4.0	4.3	560	33.2	36.1	660	74.5	74.0
461	3.9	4.0	561	29.8	31.7	661	144.8	156.9
462	4.0	3.7	562	29.0	30.6	662	210.0	250.0
463	4.1	4.5	563	28.0	30.1	663	174.4	215.2
464	4.8	4.8	564	27.2	28.8	664	112.9	136.3
465	5.1	5.1	565	27.3	29.0	665	74.1	87.0
466	5.4	5.3	566	28.5	30.9	666	49.6	58.9
467	5.7	5.6	567	28.1	29.4	667	30.4	35.0
468	5.6	5.5	568	28.5	29.9	668	19.0	21.8
469	5.8	5.6	569	28.9	30.5	669	12.5	13.6
470	5.9	5.3	570	27.9	29.1	670	9.5	10.5
471	6.2	5.8	571	27.6	28.9	671	7.9	8.8
472	6.4	6.1	572	27.4	28.6	672	7.6	9.1
473	6.2	6.1	573	27.8	28.9	673	6.4	7.6
474	6.2	6.0	574	28.6	29.9	674	5.2	5.9
475	6.8	6.9	575	30.8	33.7	675	4.8	5.2
476	7.8	7.8	576	32.7	36.2	676	4.9	4.9
477	7.7	7.7	577	33.8	37.0	677	5.9	5.8
478	7.3	6.9	578	33.1	36.1	678	7.5	6.7
479	7.3	6.9	579	32.4	35.9	679	7.8	6.8
480	7.0	7.0	580	33.4	37.4	680	6.9	6.0
481	7.1	6.9	581	35.5	41.1	681	5.3	5.0
482	7.1	6.8	582	32.8	37.0	682	4.0	4.1
483	7.2	6.7	583	29.3	32.4	683	3.0	3.0
484	7.7	6.9	584	28.2	30.7	684	2.6	2.6
485	8.2	7.7	585	28.9	31.8	685	1.8	2.2
486	9.1	8.9	586	33.2	37.2	686	1.6	1.4
487	9.2	8.8	587	41.6	48.5	687	1.2	2.2
488	9.5	8.6	588	50.4	59.8	688	1.2	1.9
489	9.6	9.9	589	61.3	72.4	689	1.2	1.8
490	10.3	10.5	590	59.6	67.3	690	1.0	2.0
491	9.9	9.6	591	54.4	60.5	691	0.7	1.6
492	9.9	9.9	592	51.1	56.4			
493	10.1	10.2	593	45.8	49.8			
494	10.1	9.5	594	41.9	47.0			
495	10.6	10.4	595	42.9	49.5			
496	12.1	12.1	596	46.2	54.4			
497	12.2	13.1	597	43.6	50.6			
498	12.0	12.4	598	36.7	40.9			
499	11.7	11.8	599	31.0	34.2			

Quantum Yields

$\phi(4)=1.0$ for $\lambda \leqslant 583$ nm.

Comments on Preferred Values

No new data have been reported on the absorption cross-sections for NO_3 radical absorption since our previous 1992 IUPAC evaluation.[3] The preferred values are based on the peak value of the cross-section at 662 nm of 2.1×10^{-17} cm^2 molecule^{-1}, adopted from the evaluation of Wayne *et al.*[4] The values of σ in the wavelength range 400–691 nm are calculated from the data of Sander,[5] normalized to the preferred peak value. The absorption cross-sections obtained by Sander[5] at 230 K in the range 400–700 nm were normalized to the value of 2.50×10^{-17} cm^2 molecule^{-1} at 662 nm to provide the preferred values given in the table for 230 K, following the recommendation of Wayne *et al.*[4] The following expression is recommended for the temperature dependence of the 662 nm band:

$$\sigma(T)=3.63\times10^{-17} - (5.13\times10^{-20}T)\ \mathrm{cm}^2\ \mathrm{molecule}^{-1}\ \text{at 662 nm}$$

The measurements of Orlando *et al.*[2] confirm qualitatively the wavelength dependence of $\phi(NO + O_2)$ and $\phi(4)$ observed in the earlier room temperature measurements of Magnotta and Johnston,[6] and provide more accurate values for $\phi(4)$. The earlier problem[6] of total quantum yields in excess of 1.4 was not encountered in the work of Orlando *et al.*,[2] which confirms that NO_3 radical dissociation is exclusively to $NO_2 + O(^3P)$ at wavelengths <585 nm.

The new molecular beam study[1] has revealed considerable new insight into the photodissociation of the NO_3 radical. There is a very sharp threshold for channel (4) at 587 nm for internally cold NO_3. Any dissociation at longer wavelengths via channel (4) must occur from photolysis of internally excited NO_3. At $\lambda \geqslant 588$ nm this process competes with photodissociation of NO_3 to form NO + O_2 via a 3-center transition state from the vibrationally excited ground state. The yield of this process falls off above 600 nm and may only occur from hot band absorption above 605 nm. These facts imply that the branching ratio for bulk, thermally equilibrated, NO_3 radicals will depend very strongly on temperature, especially near the threshold for the NO_2-forming channel, where higher temperatures will tend to favor dissociation via the simple bond fission channel (4).

The atmospheric photodissociation rates suggested by Orlando *et al.*[2] for an overhead sun at the earth's surface and the wavelength range 470–700 nm [$J(NO_2 + O) = 0.19\ s^{-1}$; $J(NO + O_2) = 0.016\ s^{-1}$] agree well with those of Magnotta and Johnston[6] which were recommended previously by IUPAC[3], i.e., $J(NO_2 + O) = 0.18 \pm 0.06\ s^{-1}$; $J(NO + O_2) = 0.022 \pm 0.007\ s^{-1}$. The new values of J are preferred for atmospheric calculations. The new knowledge from the molecular beam experiments[1] dictates that these expressions only apply for temperatures near room temperature. Further measurements of the quantum yields for NO_3 radical photolysis in bulk samples at low temperature are required before a recommendation can be made for atmospheric photolysis rates at stratospheric temperatures.

References

[1] H. F. Davis, B. Kim, H. S. Johnston, and Y. T. Lee, J. Phys. Chem. 97 2172 (1993).

[2] J. J. Orlando, G. S. Tyndall, G. K. Moortgat, and J. G. Calvert, J. Phys. Chem. **97**, 10996 (1993).

[3] IUPAC, Supplement III, 1989 (see references in Introduction).

[4] R. P. Wayne, I. Barnes, P. Biggs, J. P. Burrows, C. E. Canosa-Mas, J. Hjorth, G. Le Bras, G. K. Moortgat, D. Perner, G. Poulet, G. Restelli, and H. Sidebottom, Atmos. Environ. **25A**, 1 (1991).

[5] S. P. Sander, J. Phys. Chem. **90**, 4135 (1986).

[6] F. Magnotta and H. S. Johnston, Geophys. Res. Lett. **7**, 769 (1980).

$N_2O + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$N_2O + h\nu \rightarrow N_2 + O(^3P)$	(1)	161	742
$\rightarrow N_2 + O(^1D)$	(2)	351	341
$\rightarrow N + NO$	(3)	475	252
$\rightarrow N_2 + O(^1S)$	(4)	565	212

Preferred Values

Absorption cross-sections

λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$
175	12.6	210	0.755
180	14.6	215	0.276
185	14.3	220	0.092
190	11.1	225	0.030
195	7.57	230	0.009
200	4.09	235	0.003
205	1.95	240	0.001

Temperature dependence of absorption cross-sections

$$\ln \sigma(\lambda,T) = A_1 + A_2\lambda + A_3\lambda^2 + A_4\lambda^3 + A_5\lambda^4 + (T-300) \times \exp(B_1 + B_2\lambda + B_3\lambda^2 + B_4\lambda^3)$$

where

$A_1 = 68.21023$, $B_1 = 123.4014$,

$A_2 = -4.071805$, $B_2 = -2.116255$,

$A_3 = 4.301146 \times 10^{-2}$, $B_3 = 1.111572 \times 10^{-2}$,

$A_4 = -1.777846 \times 10^{-4}$, $B_4 = -1.881058 \times 10^{-5}$,

$A_5 = 2.520672 \times 10^{-7}$.

Quantum yields

$\phi_2 = 1.0$ for $\lambda = 185–230$ nm.

Comments on Preferred Values

The preferred absorption cross-sections and the expression for $\ln \sigma(\lambda, T)$ in (σ, T) are from Selwyn *et al.*[1] These cross-section values have been confirmed both at room temperature and at 208 K by the results of Hubrich and Stuhl[2] and Merienne *et al.*[3] who also determined the temperature dependence. Several publications with additional information on this process have appeared since the original evaluation. Selwyn and Johnston[4] studied the ultraviolet absorption spectrum of nitrous oxide and its ^{15}N isotopes over the wavelength range 172–197 nm and the temperature range 150–500 K. Lee and Suto[5] measured the photoabsorption and fluorescence cross-sections in the 106–160 nm region and studied the production and quenching of excited photofragments. Yoshino *et al.*[6] made high-resolution room temperature cross-section measurements in the 170–222 nm range. Recent state-resolved photofragment spectroscopy studies of N_2O photodissociation at 193 nm[7] and 205 nm[8] show that 43% of the energy deposited in the molecule appears as translational energy of the $O(^1D)$ atom fragment.

The preferred value of the quantum yield ($\phi_2=1.0$) is based on the results reported by Paraskevopoulos and Cvetanovic,[9] Preston and Barr,[10] and Greiner.[11] Greenblatt and Ravishankara[12] have measured the quantum yield for production of NO($^2\Pi$) and N(^{4}S) atoms at 193 nm to be $<8\times10^{-3}$.

The recommendations are unchanged from those given in the previous evaluation, IUPAC, 1992.[13]

References

[1] G. Selwyn, J. Podolske, and H. S. Johnston, Geophys. Res. Lett. **4**, 427 (1977).

[2] [illegible] Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).

[3] M. F. Merienne, B. Coquart, and A. Jenouvrier, Planet Space Sci. **38**, 617 (1990).

[4] G. S. Selwyn and H. S. Johnston, J. Chem. Phys. **74**, 3791 (1981).

[5] L. C. Lee and M. Suto, J. Chem. Phys. **80**, 4718 (1984).

[6] K. Yoshino, D. E. Freeman, and W. H. Parkinson, Planet. Space Sci. **32**, 1219 (1984).

[7] L. L. Springsteen, S. Satyapal, Y. Matsumi, L. M. Dobeck, and P. L. Houston, J. Phys. Chem. **97**, 7239 (1993).

[8] T. F. Hanisco and A. C. Kummel, J. Phys. Chem. **97**, 7242 (1993).

[9] G. Paraskevopoulos and R. J. Cvetanovic, J. Am. Chem. Soc. **91**, 7572 (1969).

[10] K. F. Preston and R. F. Barr, J. Chem. Phys. **54**, 3347 (1971).

[11] N. R. Greiner, J. Chem. Phys. **47**, 4373 (1967).

[12] G. D. Greenblatt and A. R. Ravishankara, J. Geophys. Res. **95**, 3539 (1990).

[13] IUPAC, Supplement IV, 1992 (see references in Introduction).

$N_2O_5 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$N_2O_5 + h\nu \rightarrow NO_3 + NO_2$	(1)	89	1340
$\rightarrow NO_3 + NO + O$	(2)	390	307
$\rightarrow NO_3 + NO_2^*$			
$\rightarrow NO_3 + NO_2 + h\nu$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
240–420	Harwood *et al.*, 1993[1]	(a)

Comments

(a) Measurements at 233–313 K using a dual-beam diode array spectrometer. Absolute cross-sections were based on pressure measurements and determination of NO_2 and HNO_3 impurities by UV and IR spectroscopic methods. For 260–380 nm, a pronounced temperature dependence was observed and the results were expressed in the form $\log_{10}(\sigma)=A+1000\ B/T$.

Absorption cross-section at 298 K

λ/nm	$10^{20}\sigma_{298}$/cm^2	B/K
200	920	
205	820	
210	560	
215	370	
220	220	
225	144	
230	99	
235	77	
240	62	
245	52	
250	40	
255	32	
260	26.3	−0.091
265	20.5	−0.100
270	16.5	−0.104
275	13.3	−0.112
280	11.4	−0.112
285	8.72	−0.126
290	6.80	−0.135
295	5.15	−0.152
300	3.90	−0.170
305	2.93	−0.194
310	2.19	−0.226
315	1.63	−0.253
320	1.22	−0.294
325	0.90	−0.338
330	0.68	−0.388
335	0.50	−0.409
340	0.38	−0.492
345	0.280	−0.530
350	0.217	−0.583
355	0.167	−0.719
360	0.126	−0.770
365	0.095	−0.801
370	0.074	−0.885
375	0.054	−0.765
380	0.042	−0.992
385	0.033	−0.992
390	0.0234	−0.949
395	0.0174	−0.845
400	0.0135	−0.966
405	0.0103	−1.00
410	0.0080	−1.16

Temperature dependence: $\log_{10}\sigma_T$ (cm^2 molecule^{-1})$=\log_{10}\sigma_{298}+1000\,B(1/T-1/298)$.

Quantum Yields

$\phi_1+\phi_2+\phi_3=1.0$ for
$\lambda=248\text{–}350$ nm

λ/nm	ϕ_2
248	0.72±0.17
266	0.38±0.10
287	0.21±0.05
289	0.15±0.05

Comments on Preferred Values

The new absorption cross-section values reported by Harwood *et al.*[1] show good agreement with previously recommended values,[2] which were based on the data of Yao *et al.* For wavelengths less than 280 nm, the σ values[1] are 7 lower than Yao *et al.*[3] and within 5% of the earlier values of Graham and Johnston.[4] No significant temperature dependence was observed at $\lambda\leq260$ nm,[1] but for the region 265–410 nm there is a significant temperature dependence. In general, the temperature dependence from Harwood *et al* agrees well with that of Yao *et al.*[3] except at the longer wavelengths where the new results show a slightly larger dependence, leading to σ values at 380 nm about 30% lower at 233 K than predicted from the earlier parameterization. The preferred values for the cross-section at room temperature were obtained by averaging the results from Harwood *et al.*[1] and Yao *et al.*,[3] and the temperature dependence parameters are taken from Harwood *et al.*[1]

The preferred quantum yield of unity for NO_3 radical production is based on the results of Swanson *et al.*[5] at 249 and 350 nm, those of Ravishankara *et al.*[6] at 248 nm, and those of Barker *et al.*[7] at 290 nm. The preferred quantum yield values for O atom production are those reported by Ravishankara *et al.*[6] The study of Oh *et al.*[8] indicates that electronically excited NO_2 in the $^2B_1$ state is produced, and photolysis induced fluorescence (PIF) quantum yield values are reported. For calculation of photodissociation rates in the atmosphere, channel (3) is equivalent to channel (1). In summary, it appears that NO_3 radicals are produced with unit quantum yield throughout the region 248–350 nm, and that the quantum yield for oxygen atom production decreases at longer wavelengths and appears to be approaching zero in the neighborhood of the thermodynamic threshold for O atom production at 307 nm.

References

[1] M. H. Harwood, R. L. Jones, R. A. Cox, E. Lutman, and O. V. Rattigan, J. Photochem. Photobiol. A: Chem. **73**, 167 (1993).
[2] IUPAC, Supplement III, 1989 (see references in Introduction).
[3] F. Yao, I. Wilson, and H. S. Johnston, J. Phys. Chem. **86**, 3611 (1982).
[4] R. A. Graham and H. S. Johnston, J. Phys. Chem. **82**, 254 (1978).
[5] D. Swanson, B. Kan, and H. S. Johnston, J. Phys. Chem. **88**, 3115 (1984).
[6] A. R. Ravishankara, P. H. Wine, C. A. Smith, P. E. Barbone, and A. Torabi, J. Geophys. Res. **91**, 5355 (1986).
[7] J. R. Barker, L. Brouwer, R. Patrick, M. J. Rossi, P. L. Trevor, and D. M. Golden, Int. J. Chem. Kinet. **17**, 991 (1985).
[8] D. Oh, W. Sisk, A. Young, and H. S. Johnston, J. Chem. Phys. **85**, 7146 (1986).

4.4. Organic Species

$O + CH_3 \rightarrow HCHO + H$ (1)
$\rightarrow CO + H_2 + H$ (2)

$\Delta H^\circ(1) = -285.8$ kJ·mol^{-1}
$\Delta H^\circ(2) = -287.7$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.4\pm0.3)\times10^{-10}$	294–900	Slagle, Sarzynski, and Gutman, 1987[1]	(a)
Branching Ratios			
$k_2/k=0.4\pm0.1$	298	Seakins and Leone, 1992[2]	(b)
Reviews and Evaluations			
1.4×10^{-10}	300–2500	Baulch *et al.*, 1992[3]	(c)
1.4×10^{-10}	200–900	IUPAC, 1992[4]	(d)
1.1×10^{-10}	200–300	NASA, 1994[5]	(e)

Comments

(a) Flow system with generation of CH_3 radicals and $O(^3P)$ atoms from simultaneous *in situ* photolysis of CH_3COCH_3 and SO_2, and determination of $[CH_3]$ and $[O]$ by photoionization MS. Experiments were performed under conditions such that $[O]/[CH_3]>20$, and rate coefficients were determined from the decay of CH_3 radicals. The rate coefficient k was found to be independent of pressure over the range 1–11 Torr, and its value was confirmed by measurement of the rate of formation of HCHO, the sole observable product.

(b) Laser flash photolysis with time-resolved FTIR emission from the vibrationally excited products, HCHO and CO.

(c) Based on the data of Slagle *et al.*[1]

(d) See Comments on Preferred Values.

(e) Weighted average of the measurements of Washida and Bayes,[6] Washida,[7] and Plumb and Ryan.[8]

Preferred Values

$k=1.4\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–900 K.

$k_2/k=0.4$ at 298 K.

Reliability

$\Delta\log k=\pm0.1$ at 298 K.

$\Delta(E/R)=\pm100$ K.

$\Delta(k_2/k)=\pm0.1$ at 298 K.

Comments on Preferred Values

Our previous recommendation[4] for the overall rate coefficient, based on the results of Slagle *et al.*,[1] remains unaltered. The recent experiments of Seakins and Leone[2] show that the reaction has a second channel yielding CO and, presumably, H_2 + H, and that the branching ratio for this channel is significant.

References

[1] I. R. Slagle, D. Sarzynski, and D. Gutman, J. Phys. Chem. **91**, 4375 (1987).

[2] P. W. Seakins and S. R. Leone, J. Phys. Chem. **96**, 4478 (1992).

[3] D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Frank, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. Walker, and J. Warnatz, J. Phys. Chem. Ref. Data **21**, 411 (1992).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

[6] N. Washida and K. D. Bayes, Int. J. Chem. Kinet. **8**, 777 (1976).

[7] N. Washida, J. Chem. Phys. **73**, 1665 (1980).

[8] I. C. Plumb and K. R. Ryan, Int. J. Chem. Kinet. **14**, 861 (1982).

$O(^1D) + CH_4 \rightarrow HO + CH_3$ (1)
$\rightarrow O(^3P) + CH_4$ (2)
$\rightarrow HCHO + H_2$ (3)

$\Delta H^\circ(1)=-178.8$ kJ·mol^{-1}
$\Delta H^\circ(2)=-189.7$ kJ·mol^{-1}
$\Delta H^\circ(3)=-472.7$ kJ·mol^{-1}

No new data have been published on the overall k or the branching ratio of this reaction since our last evaluation.

Preferred Values ($k = k_1 + k_2 + k_3$)

$k = 1.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

$k_1/k = 0.9$; $k_3/k = 0.1$; $k_2/k = 0$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta k_1/k = \Delta k_3/k = \pm 0.1$ over the temperature range 200–300 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

This data sheet is largely based on our previous evaluation,[1] but includes additional comments from a later evaluation.[2] The most recent data[3] on this reaction are in excellent agreement with the previous recommendation,[2] which is unaltered. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4] Casavecchia *et al.*[5] have carried out a molecular beam study which indicates an alternative reaction channel yielding CH_3O (or CH_2OH) + H. Further work is needed to confirm this observation.

A study[6] of the 248 nm laser flash photolysis of O_3-CH mixtures, with low-pressure FTIR emission spectroscopy to monitor the HO product, has provided evidence that the partitioning of energy in the vibrationally excited HO radicals (up to $n=4$, the maximum allowable according to the energetics of the reaction) is non-statistical.

References

[1] CODATA, Supplement II, 1984 (see references in Introduction).

[2] IUPAC, Supplement III, 1989 (see references in Introduction).

[3] P. H. Wine and A. R. Ravishankara, Chem. Phys. **69**, 365 (1982).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

[5] P. Casavecchia, R. J. Buss, S. J. Sibener, and Y. T. Lee, J. Chem. Phys. **73**, 6351 (1980).

[6] P. M. Aker, J. J. A. O'Brien, and J. J. Sloan, J. Chem. Phys. **84**, 74 (1986).

$HO + CH_4 \rightarrow H_2O + CH_3$

$\Delta H° = -60.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.0 \times 10^{-12} \exp[-(1944 \pm 114)/T]$	278–378	Finlayson-Pitts *et al.*, 1992[1]	(a)
5.87×10^{-15}	298		
$(2.62 \pm 0.27) \times 10^{-14}$	378	Lancar, Le Bras, and Poulet, 1992[2]	(b)
$(4.27 \pm 0.18) \times 10^{-14}$	422		
$< 3 \times 10^{-16}$	178	Sharkey and Smith, 1993[3]	(c)
$(1.65 \pm 0.2) \times 10^{-15}$	216		
$(7.6 \pm 0.3) \times 10^{-15}$	298		
$9.65 \times 10^{-20}\, T^{2.58} \exp(-1082/T)$	293–800	Dunlop and Tully, 1993[4]	(c,d)
$(5.62 \pm 0.43) \times 10^{-15}$	293		
$(5.4 \pm 0.2) \times 10^{-15}$	292	Saunders *et al.*, 1994[5]	(c)
$2.56 \times 10^{-12} \exp[-(1765 \pm 146)/T]$	233–343	Mellouki *et al.*, 1994[6]	(c)
$(6.34 \pm 0.88) \times 10^{-15}$	298		
Reviews and Evaluations			
$3.9 \times 10^{-12} \exp(-1885/T)$	240–300	IUPAC, 1992[7]	(e)
$7.44 \times 10^{-18}\, T^2 \exp(-1361/T)$	223–1512	Atkinson, 1994[8]	(f)
$2.65 \times 10^{-12} \exp(-1800/T)$	223–400	NASA, 1994[9]	(g)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO radicals.

(b) Discharge flow system with EPR detection of HO radicals.

(c) Pulsed laser photolysis system with LIF detection of HO radicals.

(d) The temperature-dependent expression cited[4] is that for the rate coefficients of Dunlop and Tully[4] combined with those of Vaghjiani and Ravishankara[10] and as such covers the temperature range 223–800 K[4].

(e) Derived from the absolute rate coefficient data of Dixon-Lewis and Williams,[11] Margitan *et al.*,[12] Howard and Evenson,[13] Ernst *et al.*,[14] Tully and Ravishankara,[15] Madronich and Felder,[16] Smith *et al.*,[17] Bott and Cohen,[18] and Vaghjiani and Ravishankara.[10] The three parameter equation $k = CT^2 \exp(-D/T)$ was fitted to these data,[10-18] resulting in $k = 7.44 \times 10^{-18}\, T^2 \exp(-1355/T)$ cm^3 molecule^{-1} s^{-1} over the range 223–1512 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, was centered at 265 K and was derived from the three parameter equation with $A = C\, e^2\, T^2$ and $B = D + 2T$.

Derived from the absolute rate coefficient data of Dixon-Lewis and Williams,[11] Margitan *et al.*,[12] Howard and Evenson,[13] Ernst *et al.*,[14] Tully and Ravishankara,[15] Madronich and Felder,[16] Smith *et al.*,[17] Bott and Cohen,[18] Vaghjiani and Ravishankara,[10] and Finlayson-Pitts *et al.*,[1] using the three parameter expression $k=CT^2 \exp(-D/T)$.

The 298 K rate coefficient is based on the absolute rate coefficient data of Vaghjiani and Ravishankara,[10] Finlayson-Pitts *et al.*,[1] Dunlop and Tully,[4] Saunders *et al.*,[5] and Mellouki *et al.*,[6] and the temperature dependence is derived from those of Vaghjiani and Ravishankara,[10] Finlayson-Pitts *et al.*,[1] Dunlop and Tully,[4] and Mellouki *et al.*[6] at temperatures <400 K.

Preferred Values

$k=6.2\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=2.3\times10^{-12}\exp(-1765/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k=\pm0.08$ at 298 K

$\Delta(E/R)=\pm100$ K.

Comments on Preferred Values

The absolute rate coefficients of Finlayson-Pitts *et al.*,[1] Dunlop and Tully,[4] and Mellouki *et al.*[6] are in good agreement with those of Vaghjiani and Ravishankara.[10] However, over the temperature range ~250–420 K these rate coefficients of Vaghjiani and Ravishankara,[10] Finlayson-Pitts *et al.*,[1] Dunlop and Tully,[4] and Mellouki *et al.*[6] are ~20% lower than most of the previously reported absolute rate coefficients.[8,9] While Vaghjiani and Ravishankara[10] concluded that a number of earlier studies[19–21] gave rise to erroneously high measured rate coefficients due to the use of lower CH_4/OH concentration ratios and the occurrence of secondary reactions, Finlayson-Pitts *et al.*[1] used a CH_4/OH concentration ratio significantly lower than employed by Vaghjiani and Ravishankara.[10]

The preferred values are derived from the absolute rate coefficient data of Vaghjiani and Ravishankara[10] and Dunlop and Tully,[4] both conducted over significant, and overlapping, temperature ranges. The temperature-dependent expression obtained by Dunlop and Tully[4] from a fit of their data[4] and those of Vaghjiani and Ravishankara[10] to the three parameter equation $k=CT^n\exp(-D/T)$ is accepted, of $k=9.65\times10^{-20}T^{2.58}\exp(-1082/T)$ cm^3 molecule^{-1} s^{-1} over the range 223–800 K. The preferred Arrhenius expression, $k=A\times\exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A=Ce^nT^n$ and $B=D+nT$. The recommended three-parameter expression leads to a calculated rate coefficient at 1234 K which is within 15% of the value measured by Bott and Cohen.[18]

The absolute rate coefficients of Lancar *et al.*[2] at 378 and 422 K and of Sharkey and Smith[3] and Saunders *et al.*[5] at 298 K are within 25% of the preferred values, and the upper limit obtained by Sharkey and Smith[3] at 178 K is also consistent with the rate coefficient calculated from the preferred rate coefficient expression. However, the rate coefficient reported by Sharkey and Smith[3] at 216 K is a factor of 2.5 higher than that calculated from the preferred Arrhenius expression.

References

[1] B. J. Finlayson-Pitts, M. J. Ezell, T. M. Jayaweera, H. N. Berko, and C. C. Lai, Geophys. Res. Lett. **19**, 1371 (1992).

[2] I. T. Lancar, G. Le Bras, and G. Poulet, C. R. Acad. Sci. Paris, Series II, 1487 (1992).

[3] P. Sharkey and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **89**, 631 (1993).

[4] J. R. Dunlop and F. P. Tully, J. Phys. Chem. **97**, 11148 (1993).

[5] S. M. Saunders, K. J. Hughes, M. J. Pilling, D. L. Baulch, and P. I. Smurthwaite, Proc. SPIE **1715**, 88 (1993).

[6] A. Mellouki, S. Téton, G. Laverdet, A. Quilgars, and G. Le Bras, J. Chim. Phys. **91**, 473 (1994).

[7] IUPAC Supplement IV, 1992 (see references in Introduction).

[8] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[9] NASA Evaluation No. 11, 1994 (see references in Introduction).

[10] G. L. Vaghjiani and A. R. Ravishankara, Nature **350**, 406 (1991)

[11] G. Dixon-Lewis and A. Williams, *11th International Symposium on Combustion, 1966* (The Combustion Institute, 1967), pp. 951–958.

[12] J. J. Margitan, F. Kaufman, and J. G. Anderson, Geophys. Res. Lett. **1**, 80 (1974).

[13] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).

[14] J. Ernst, H. Gg. Wagner, and R. Zellner, Ber. Bunsenges Phys. Chem. **82**, 409 (1978).

[15] F. P. Tully and A. R. Ravishankara, J. Phys. Chem. **84**, 3126 (1980).

[16] S. Madronich and W. Felder, *20th International Symposium on Combustion, 1984* (The Combustion Institute), pp. 703–713 (1985).

[17] G. P. Smith, P. W. Fairchild, J. B. Jeffries, and D. R. Crosley, J. Phys. Chem. **89**, 1269 (1985).

[18] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **21**, 485 (1989).

[19] N. R. Greiner, J. Chem. Phys. **53**, 1070 (1970).

[20] D. D. Davis, S. Fischer, and R. Schiff, J. Chem. Phys. **61**, 2213 (1974).

[21] K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).

$HO + C_2H_2 + M \rightarrow C_2H_2OH + M$

$\Delta H^\circ = -152\ kJ \cdot mol^{-1}$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 5 \times 10^{-30} (T/300)^{-1.5} [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298K.

$\Delta n = \pm 1.5$.

Comments on Preferred values

The preferred 298 K rate coefficient is based on the experimental data of Schmidt *et al.*[1] and Wahner and Zetzsch and the theoretical analysis of Smith *et al.*,[3] and the temperature dependence is based on the data of Perry *et al.*,[4] Michael *et al.*,[5] and Perry and Williamson,[6] as discussed and evaluated by Atkinson.[7] At temperatures above ~500 K another component of the rate coefficient with a much stronger temperature dependence also has to be taken into account.[7] The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[8]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.0 \pm 1.5) \times 10^{-13}$	297	Arnts, Seila, and Bufalini, 1989[9]	(a)
Reviews and Evaluations			
$9.0 \times 10^{-13} (T/300)^2$	200–300	IUPAC, 1992[8]	(b)
$8.3 \times 10^{-13} (T/300)^2$	220–300	NASA, 1994[10]	(c)
$9.4 \times 10^{-12} \exp(-700/T)$	230–500	Atkinson, 1994[11]	(d)

Comments

(a) HO radicals were generated by the photolysis of methyl nitrite in the presence of NO. The concentrations of C_2H_2 and C_2H_6 were measured by GC. The rate coefficient k was measured relative to that of the reaction $HO + C_2H_6 \rightarrow H_2O + C_2H_5$, using a rate coefficient of $k(HO + C_2H_6) = 2.46 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation). Experiments were carried out in 760 Torr of air.

(b) See Comments on Preferred Values.

(c) Based on the analysis of Smith *et al.*[3]

(d) The previous recommendations[7] were unchanged.

Preferred Values

$k_\infty = 9.0 \times 10^{-13} (T/300)^2$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.1$ at 298 K.

$\Delta n = \sim 1$.

Comments on Preferred Values

The preferred values are based on the evaluation of Atkinson[7] of the experimental data of Perry *et al.*,[4] Michael *et al.*,[5] Perry and Williamson,[6] Atkinson and Aschmann,[12] Schmidt *et al.*,[1] Wahner and Zetzsch,[2] Hatakeyama *et al.*[13] and Liu *et al.*[14] Falloff curves are constructed with $F_c = 0.69$ at 228 K and 0.62 at 298 K, as derived by Smith *et al.*[3] The preferred values are identical to those in our previous evaluation, IUPAC, 1992,[8] and the rate coefficient of Arnts *et al.*[9] at room temperature and atmospheric pressure of air is in good agreement with the preferred values.

Intermediate falloff range

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	P/Torr	M	Temp./K	Reference	Comments
Absolute Rate Coefficients					
[illegible] $10^{-13}\exp[(1460\pm500)/T]$	414–864	He	627–713	Lai, Hsu, and Lee, 1992[15]	(a)

Comments

(a) HO radicals were formed by 193 nm photolysis of N_2O in the presence of H_2O, and monitored by LIF at 310 nm. The rate coefficients for the forward and reverse $\{k = (2.2\pm0.4)\times10^{12}\exp[-(15100\pm600)]\ s^{-1}\}$ reactions did not change appreciatively with pressure, although they had not reached the high pressure limit. From the temperature dependence of the equilibrium constant, a value of $\Delta H^\circ_0 = -(140.6\pm5.0)$ kJ mol^{-1} was derived.

References

[1] V. Schmidt, G. Y. Zhu, K. H. Becker, and E. H. Fink, Ber. Bunsenges. Phys. Chem. **89**, 321 (1985).

[2] A. Wahner and C. Zetzsch, Ber. Bunsenges. Phys. Chem. **89**, 323 (1985).

[3] G. P. Smith, P. W. Fairchild, and D. R. Crosley, J. Chem. Phys. **81**, 2667 (1984).

[4] R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. **67**, 5577 (1977).

[5] J. V. Michael, D. F. Nava, R. P. Borkowski, W. A. Payne, and L. J. Stief, J. Chem. Phys. **73**, 6108 (1980).

[6] R. A. Perry and D. Williamson, Chem. Phys. Lett. **93**, 331 (1982).

[7] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 1**, 1 (1989).

[8] IUPAC, Supplement IV, 1992 (see references in Introduction).

[9] R. R. Arnts, R. L. Seila, and J. J. Bufalini, J. Air Pollut. Control Assoc. **39**, 453 (1989).

[10] NASA Evaluation No. 11, 1994 (see references in Introduction).

[11] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[12] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **16**, 259 (1984).

[13] S. Hatakeyama, N. Washida, and H. Akimoto, J. Phys. Chem. **90**, 173 (1986).

[14] A. Liu, W. A. Mulac, and C. D. Jonah, J. Phys. Chem. **92**, 5942 (1988).

[15] L. H. Lai, Y. C. Hsu, and Y.-P. Lee, J. Chem. Phys. **97**, 3092 (1992).

$HO + C_2H_4 + M \rightarrow C_2H_4OH + M$

$\Delta H^\circ = -126$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$7\times10^{-29}(T/300)^{-3.1}$ [N_2]	200–300	IUPAC, 1992[1]	(a)
$1.0\times10^{-28}(T/300)^{-0.8}$ [air]	200–300	NASA, 1994[2]	(b)
$3.0\times10^{-29}(T/300)^{-4}$ [He]	295–420	Atkinson, 1994[3]	(c)
$6\times10^{-29}(T/300)^{-4}$ [N_2, O_2]	295–420		

Comments

(a) Based on a series of earlier data. Because of the smallest scatter, heavier weight was given to the results of Ref. 4. Falloff extrapolation was carried out with a calculated value of $F_c=0.7$ from Ref. 5.

(b) Based on a series of earlier data, in particular on the data of Ref. 5.

(c) Detailed review of all available earlier data. The temperature dependence based on the work of Kuo and Lee[4] and a previous evaluation[6] was adopted.

Preferred Values

$k_0=7\times10^{-29}\ (T/300)^{-3.1}\ [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_0 = \pm0.3$ at 298 K.

$\Delta n = \pm2$.

Comments on Preferred Values

No new measurements have been reported. The values recommended by Atkinson[3] in a recent review are similar to those preferred earlier.[1]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Commen
Absolute Rate Coefficients			
$(7.7\pm1.0)\times10^{-12}$	298	Becker, Geiger, and Wiesen, 1991[7]	(a)
Reviews and Evaluations			
9.0×10^{-12}	200–300	IUPAC, 1992[1]	(b)
8.8×10^{-12}	200–300	NASA, 1994[2]	(c)
$9.0\times10^{-12}(T/300)^{-1.1}$	290–525	Atkinson, 1994[3]	(d)

Comments

(a) HO radicals were generated by 248 nm laser photolysis of H_2O_2 and monitored in real time by LIF at 308 nm. Experiments were carried out at a total pressure of 760 Torr of synthetic air. Numerical simulation with a mechanism formed by 12 reactions.

(b) Based on results from Ref. 8 which are in good agreement with the value preferred earlier. The temperature coefficient is uncertain because of extensive falloff at temperatures above 300 K and the possibility of a small activation barrier.

(c) See comment (b) for k_0.

(d) The previous recommendations[6] were unchanged.

Preferred Values

$k_\infty=9\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of tem perature over the range 200–300 K.

Reliability

$\Delta\log k_\infty=\pm0.3$ at 298 K.

$\Delta n=\pm0.5$.

Comments on Preferred Values

The preferred value is similar to those reported in Refs. 3 and 6. The temperature dependence is uncertain due to the possibility of a small electronic barrier. These preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.[1]

Intermediate falloff range

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	P/Torr	M	Temp./K	Reference	Comments
Relative Rate Coefficients					
4.4×10^{-12}	790	Ar	1197	Bott and Cohen, 1991[9]	(a)
$4.3\times10^{-13}\exp[(1200\pm800)/T]$	500–616	He	544–590	Diau and Lee, 1992[10]	(b)

Comments

(a) Shock wave experiments. HO radicals were generated by dissociation of *t*-butyl hydroperoxide and detected by UV absorption at 309 nm.

(b) HO radicals were generated by photolysis of N_2O in the presence of H_2O at 193 nm and detected by LIF at 310 nm. Experiments were carried out between 544–673 K and 276–616 Torr He.

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[4] C.-H. Kuo and Y.-P. Lee, J. Phys. Chem. **95**, 1253 (1991).

[5] Th. Klein, J. Barnes, K. H. Becker, E. H. Fink, and F. Zabel, J. Phys. Chem. **88**, 5020 (1984).

[6] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 1**, 1 (1989).

[7] K. H. Becker, H. Geiger, and P. Wiesen, Chem. Phys. Lett. **184**, 256 (1991).

[8] O. J. Nielsen, O. Jørgensen, M. Donlon, H. W. Sidebottom, D. J. O'Farrell, and J. Treacy, Chem. Phys. Lett. **168**, 319 (1990).

[9] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **23**, 1075 (1991).

[10] E. W.-G. Diau and Y.-P. Lee, J. Chem. Phys. **96**, 377 (1992).

$HO + C_2H_6 \rightarrow H_2O + C_2H_5$

$\Delta H° = -75.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$([illegible].34\pm0.40)\times10^{-13}$	298	Dóbé *et al.*, 1991,[1] 1992[2]	(a)
$(1.34\pm0.24)\times10^{-11}$	1225	Bott and Cohen, 1991[3]	(b)
$(1.1\pm0.2)\times10^{-14}$	138	Sharkey and Smith, 1993[4]	(c)
$([illegible].3\pm0.3)\times10^{-14}$	178		
$([illegible]\pm0.4)\times10^{-14}$	216		
$([illegible].93\pm0.14)\times10^{-13}$	298		
$1.03\times10^{-11}\exp[-(1108\pm40)/T]$	231–377	Talukdar *et al.*, 1994[5]	(c)
$([illegible].43\pm0.13)\times10^{-13}$	298		
Relative Rate Coefficients			
$[illegible].5\times10^{-12}\exp(-943/T)$	298–373	Finlayson-Pitts, Hernandez, and Berko, 1993[6]	(d)
$[illegible].76\times10^{-13}$	298		
Reviews and Evaluations			
$7.8\times10^{-12}\exp(-1020/T)$	240–300	IUPAC, 1992[7]	(e)
$1.51\times10^{-17}T^2\exp(-492/T)$	226–800	Atkinson, 1994[8]	(f)
$8.7\times10^{-12}\exp(-1070/T)$	226–298	NASA, 1994[9]	(g)

Comments

(a) Pulsed laser photolysis system with resonance fluorescence detection of HO radicals.

(b) HO radicals were generated from the thermal decomposition of *t*-butyl hydroperoxide in a shock tube and monitored by UV absorption at 309 nm.

(c) Pulsed laser photolysis system with LIF detection of HO radicals.

(d) Relative rate method. HO radicals were generated from the photolysis of O_3-H_2O-ethane-propane mixtures and from the dark reactions of O_3 in the presence of ethane and propane.[6] The rate coefficient ratios k(HO + ethane)/k(HO + propane) were placed on an absolute basis using a rate coefficient of k(HO + propane) $=8.0\times10^{-12}\exp(-590/T)$cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) Derived using the absolute rate coefficient data of Howard and Evenson,[10] Leu,[11] Margitan and Watson,[12] Tully *et al.*,[13,14] Smith *et al.*,[15] Baulch *et al.*,[16] Devolder *et al.*,[17] Stachnick *et al.*,[18] Wallington *et al.*,[19] Bourmada *et al.*,[20] Zabarnick *et al.*,[21] and Abbatt *et al.*[22] The absolute rate coefficient data used in the evaluation[10–22] were fitted to the three parameter equation $k=CT^2\exp(-D/T)$, resulting in $k=1.51\times10^{-17}T^2\exp(-492/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 226–800 K. The Arrhenius expression, $k=A\exp(-B/T)$, was centered at 265 K and was derived from the three parameter equation with $A=C\,e^2\,T^2$ and $B=D+2T$.

(f) Derived from the absolute rate coefficient data of Howard and Evenson,[10] Leu,[11] Margitan and Watson,[12] Tully *et al.*,[13,14] Smith *et al.*,[15] Baulch *et al.*,[16] Devolder *et al.*,[17] Stachnik *et al.*,[18] Wallington *et al.*,[19] Bourmada *et al.*,[20] Zabarnick *et al.*,[21] and Abbatt *et al.*[22] These data were fitted to the three parameter equation $k=CT^2\exp(-D/T)$.

(g) The 298 K rate coefficient was derived from the data of Tully *et al.*,[14] Wallington *et al.*,[19] Abbatt *et al.*,[22] Schiffman *et al.*,[23] Talukdar *et al.*,[5] and Anderson and Stephens (unpublished data, 1994), using a temperature dependence of $E/R=1070$ K to recalculate the reported room temperature data to 298 K. The temperature dependence was derived from the data of Wallington *et al.*,[19] Talukdar *et al.*,[5] and Anderson and Stephens (unpublished data, 1994).

Preferred Values

$k=2.5\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=7.9\times10^{-12}\exp(-1030/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k=\pm0.10$ at 298 K.

$\Delta(E/R)=\pm100$ K.

Comments on Preferred Values

The absolute rate coefficients of Dóbé *et al.*,[1,2] Bott and Cohen[3] (from an apparently limited study), Sharkey and Smith,[4] and Talukdar *et al.*[5] and the relative rate coefficients of Finlayson-Pitts *et al.*[6] are in good agreement (within 20% except for the 138 K rate coefficient of Sharkey and Smith[4]) with the three-parameter expression obtained in the previous IUPAC evaluation.[7] The preferred values were obtained by using the absolute rate coefficient data of Howard and Evenson,[10] Leu,[11] Margitan and Watson,[12] Tully *et al.*,[13,14] Smith *et al.*,[15] Baulch *et al.*,[16] Devolder *et al.*,[17] Stachnick *et al.*,[18] Wallington *et al.*,[19] Bourmada *et al.*,[20] Zabarnick *et al.*,[21] Abbatt *et al.*,[22] and Talukdar *et al.*[5]

The absolute rate coefficient data used in the evaluation[5,10–22] were fitted to the three parameter equation $k=CT^2 \times \exp(-D/T)$, resulting in $k=1.52\times10^{-17}\ T^2\ \exp(-499/T)$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ over the temperature range 226–800 K. The preferred Arrhenius expression, $k=A\ \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A=C\ e^2\ T^2$ and $B=D+2T$. The room temperature (the temperature not being specified) absolute rate coefficient of Schiffman *et al.*[23] is in good agreement with the preferred 298 K rate coefficient, as are the relative rate coefficients of Baulch *et al.*[24] and Edney *et al.*[25]

References

[1] S. Dóbé, T. Turányi, T. Bérces, and F. Márta, Proc. Indian Acad. Sci. (Chem. Sci.) **103**, 499 (1991).

[2] S. Dóbé, T. Turányi, A. A. Iogansen, and T. Bérces, Int. J. Chem. Kinet. **24**, 291 (1992).

[3] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **23**, 1017 (1991).

[4] P. Sharkey and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **89**, 631 (1993).

[5] R. K. Talukdar, A. Mellouki, T. Gierczak, S. Barone, S.-Y. Chiang, and A. R. Ravishankara, Int. J. Chem. Kinet. **26**, 973 (1994).

[6] B. J. Finlayson-Pitts, S. K. Hernandez, and H. N. Berko, J. Phys. Chem. **97**, 1172 (1993).

[7] IUPAC Supplement IV, 1992 (see references in Introduction).

[8] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[9] NASA Evaluation No. 11, 1994 (*see references in Introduction*).

[10] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 4303 (1976).

[11] M.-T. Leu, J. Chem. Phys. **70**, 1662 (1979).

[12] J. J. Margitan and R. T. Watson, J. Phys. Chem. **86**, 3819 (1982).

[13] F. P. Tully, A. R. Ravishankara, and K. Carr, Int. J. Chem. Kinet. **15**, 1 (1983).

[14] F. P. Tully, A. T. Droege, M. L. Koszykowski, and C. F. Melius, J. Ph Chem. **90**, 691 (1986).

[15] C. A. Smith, L. T. Molina, J. J. Lamb, and M. J. Molina, Int. J. Che Kinet. **16**, 41 (1984).

[16] D. L. Baulch, I. M. Campbell, and S. M. Saunders, J. Chem. Soc. Farad. Trans. **81**, 259 (1985).

[17] P. Devolder, M. Carlier, J. F. Pauwels, and L. R. Sochlet, Chem. Phy Lett. **111**, 94 (1984).

[18] R. A. Stachnik, L. T. Molina, and M. J. Molina, J. Phys. Chem. **90**, 27 (1986).

[19] T. J. Wallington, D. M. Neuman, and M. J. Kurylo, Int. J. Chem. Kin **19**, 725 (1987).

[20] N. Bourmada, C. Lafage, and P. Devolder, Chem. Phys. Lett. **136**, 2 (1987).

[21] S. Zabarnick, J. W. Fleming, and M. C. Lin, Int. J. Chem. Kinet. **20**, 1 (1988).

[22] J. P. D. Abbatt, K. L. Demerjian, and J. G. Anderson, J. Phys. Chem. 94 4566 (1990).

[23] A. Schiffman, D. D. Nelson, Jr., M. S. Robinson, and D. J. Nesbitt. J Phys. Chem. **95**, 2629 (1991).

[24] D. L. Baulch, R. J. B. Craven, M. Din, D. D. Drysdale, S. Grant, D. J Richardson, A. Walker, and G. Watling, *J. Chem. Soc. Faraday Trans.* **79**, 689 (1983).

[25] E. O. Edney, T. E. Kleindienst, and E. W. Corse, Int. J. Chem. Kinet. 18 1355 (1986).

$HO + C_3H_6 + M \rightarrow C_3H_6OH + M$

$\Delta H° = -134\ \mathrm{kJ{\cdot}mol^{-1}}$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 8\times10^{-27}\ (T/300)^{-3.5}\ [N_2]\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 1.0$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The uncertainty of the extrapolated k_0 is large, because the reaction is close to the high-pressure limit at pressures of 1 bar. The preferred values follow the falloff extrapolations from Refs. 1 and 2 which show the smallest scatter. Falloff extrapolations are made using $F_c=0.5$ at 300 K. The temperature coefficient of k_0 is estimated by analogy to the reaction $HO + C_2H_4 + M \rightarrow C_2H_4OH + M$. The recommendation of our previous evaluation, IUPAC, 1992[3] are unchanged.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 3.0\times10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.1$ over the temperature range 200–300 K.

$\Delta n = \pm 1$.

on Preferred Values

preferred values are based on Refs. 1, 2, and 4–7. an uncertainty about the extent of falloff at temperatures above 300 K and there is the possibility of a small barrier, as in the reaction HO + C_2H_2 + M OH + M. We here prefer a temperature independent k, in contrast to the recommendation of Ref. 8. The recommendations of our previous evaluation, IUPAC, 1992,[3] changed.

References

[1] Th. Klein, I. Barnes, K. H. Becker, E. H. Fink, and F. Zabel, J. Phys. Chem. **88**, 5020 (1984).
[2] R. Zellner and K. Lorenz, J. Phys. Chem. **88**, 984 (1984).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] CODATA, Supplement II, 1984 (see references in Introduction).
[5] IUPAC, Supplement III, 1989 (see references in Introduction).
[6] O. J. Nielsen, O. Jorgensen, M. Donlon, H. W. Sidebottom, D. J. O'Farrell, and J. Treacy, Chem. Phys. Lett. **168**, 319 (1990).
[7] F. P. Tully and J. E. M. Goldsmith, Chem. Phys. Lett. **116**, 345 (1985).
[8] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

$HO + C_3H_8 \rightarrow H_2O + n\text{-}C_3H_7$ (1)
$\rightarrow H_2O + i\text{-}C_3H_7$ (2)

$9.1\ \mathrm{kJ\cdot mol^{-1}}$
$86.6\ \mathrm{kJ\cdot mol^{-1}}$

Rate coefficient data ($k=k_1+k_2$)

molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Rate Coefficients			
$30)\times 10^{-12}$	298	Dóbé *et al.*, 1991[1]	(a)
$10^{-12}\exp[-(650\pm30)/T]$	233–363	Mellouki *et al.*, 1994[2]	(b)
$09)\times 10^{-12}$	295		
$10^{-11}\exp[-(657\pm46)/T]$	233–376	Talukdar *et al.*, 1994[3]	(b)
$04)\times 10^{-12}$	298		
Rate Coefficients			
$05)\times 10^{-12}$	298±2	Nielsen *et al.*, 1994[4]	(c)
$06)\times 10^{-12}$	298	Finlayson-Pitts, Hernandez, and Berko, 1993[5]	(d)
$19)\times 10^{-12}$	298	Finlayson-Pitts, Hernandez, and Berko, 1993[5]	(e)
and Evaluations			
$10^{-12}\exp(-640/T)$	270–340	IUPAC, 1992[6]	(f)
$10^{-17}T^2\exp(-44/T)$	293–1220	Atkinson, 1994[7]	(g)
$10^{-11}\exp(-660/T)$	200–300	NASA, 1994[8]	(h)

Comments

Pulsed laser photolysis system with resonance fluorescence detection of HO radicals.

Pulsed laser photolysis system with LIF detection of HO radicals.

Relative rate method. HO radicals generated by the dark reaction of N_2H_4 with O_3 in air. The concentrations of propane and 2-methylpropane were measured during the experiments by GC and a rate constant ratio of k(OH + propane)/k(OH + 2-methylpropane)=0.47 ± 0.02 determined. This rate constant ratio is placed on an absolute basis by use of k(OH + 2-methylpropane) 2.33×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.[7]

Relative rate method. HO radicals generated by the photolysis of O_3-H_2O-O_2 mixtures and by the dark reaction of O_3-propane-n-butane-H_2O-O_2 mixtures. The propane and n-butane concentrations were measured during the experiments by GC and rate constant ratios of k(OH + propane)/k(OH + n-butane)=0.452±0.023 and 0.453±0.021 were obtained for the photolytic and dark reactions, respectively. These rate constant ratios are placed on an absolute basis by use of k(n-butane) =2.54×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.[7]

(e) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures, photolysis of O_3-H_2O-O_2 mixtures, and the dark reaction of O_3-propane-2-methylpropane-H_2O-O_2 mixtures. The concentrations of propane and 2-methylpropane were measured during the experiments by GC. Rate constant ratios k(OH + propane)/k(OH + 2-methylpropane) of 0.448±0.026, 0.522±0.015 and 0.496±0.025, respectively, were obtained. The average of these rate constant ratios is placed on an absolute basis by use of k(2-methylpropane)=2.33×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.[7]

(f) Derived from the absolute rate coefficient data of Greiner,[9] Bott and Cohen,[10] Smith *et al.*,[11] Baulch *et al.*,[12] Droege and Tully,[13] Abbatt *et al.*,[14] and Mac Leod *et al.*[15] and the relative rate coefficients of Baker *et al.*[16,17] and Atkinson *et al.*[18] These data[9–18] were fitted to the three parameter equation $k=CT^2\exp(-D/T)$, resulting in $k=1.48\times10^{-17}\ T^2\exp(-39/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 293–1220 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$, was centered at 300 K, and was derived from the three parameter equation with $A=C\ e^2\ T^2$ and $B=D+2T$.

(g) Derived from the absolute rate coefficient data of Greiner,[9] Bott and Cohen,[10] Smith *et al.*,[11] Baulch *et al.*,[12] Droege and Tully,[13] Abbatt *et al.*,[14] and Mac Leod *et al.*[15] and the relative rate coefficients of Baker *et al.*[16,17] and Atkinson *et al.*[18] These data[9–18] were fitted to the three parameter equation $k=CT^2\times\exp(-D/T)$.

(h) The room temperature rate coefficients of Greiner,[9] Bradley *et al.*,[19] Tully *et al.*,[20] Baulch *et al.*,[12] Schmidt *et al.*,[21] Droege and Tully,[13] Abbatt *et al.*,[14] Schiffman *et al.*,[22] Talukdar *et al.*,[3] Mellouki *et al.*,[2] and Anderson and Stephens (unpublished data, 1994) were used to derive the 298 K value. The temperature dependence was derived from a least-squares analysis of the rate coefficients of Droege and Tully[13] at temperatures <400 K, Talukdar *et al.*[3] Mellouki *et al.*,[2] and Anderson and Stephens (unpublished data, 1994), with the A factor being adjusted to fit the 298 K value.

Preferred Values

$k=1.10\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=8.0\times10^{-12}\exp(-590/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k=\pm0.08$ at 298 K.
$\Delta(E/R)=\pm150$ K.

Comments on Preferred Values

The room temperature absolute and relative rate coefficients of Dóbé *et al.*,[1] Mellouki *et al.*,[2] Talukdar *et al.*,[3] Nielsen *et al.*,[4] and Finlayson-Pitts *et al.*[5] are in good[1] or excellent[2–5] agreement with the previous IUPAC evaluation.[6] The absolute rate coefficient data of Greiner,[9] Bott and Cohen,[10] Smith *et al.*,[11] Baulch *et al.*,[12] Droege and Tully,[13] Abbatt *et al.*,[14] Mac Leod *et al.*,[15] Mellouki *et al.*,[2] and Talukdar *et al.*[3] and the relative rate coefficients of Baker *et al.*[16,17] and Atkinson *et al.*[18] were used to derive the preferred value. These data were fitted to the three-parameter equation $k=CT^2\exp(-D/T)$, resulting in $k=1.54\times10$ $T^2\exp(-60/T)$ cm^3 molecule^{-1} s^{-1} over the range 23 1220 K. The preferred Arrhenius expression, $k=A\exp($- $T)$, is centered at 265 K, and is derived from the three p rameter equation with $A=C\ e^2\ T^2$ and $B=D+2T$. Th relative rate coefficients of Baulch *et al.*[23] and Edney *et al* are in good agreement with the recommended expression. is the absolute rate coefficient of Schiffman *et al.*[22] at roo temperature (which was not specified).

References

[1] S. Dóbé, T. Turányi, T. Bérces, and F. Márta, Proc. Indian Acad. S (Chem. Sci.) **103**, 499 (1991).
[2] A. Mellouki, S. Téton, G. Laverdet, A. Quilgars, and G. Le Bras, J. Ch Phys. **91**, 473 (1994).
[3] R. K. Talukdar, A. Mellouki, T. Gierczak, S. Barone, S.-Y. Chiang, an A. R. Ravishankara, Int. J. Chem. Kinet. **26**, 973 (1994).
[4] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Int. J. Ch Kinet. **23**, 1095 (1991).
[5] B. J. Finlayson-Pitts, S. K. Hernandez, and H. N. Berko, J. Phys. Ch **97**, 1172 (1993).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).
[7] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[8] NASA Evaluation No. 11, 1994 (see references in Introduction).
[9] N. R. Greiner, J. Chem. Phys. **53**, 1070 (1970).
[10] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **16**, 1557 (1984).
[11] G. P. Smith, P. W. Fairchild, J. B. Jeffries, and D. R. Crosley, J. Phy Chem. **89**, 1269 (1985).
[12] D. L. Baulch, I. M. Campbell, and S. M. Saunders, J. Chem. Soc. Farada Trans. 1, **81**, 259 (1985).
[13] A. T. Droege and F. P. Tully, J. Phys. Chem. **90**, 1949 (1986).
[14] J. P. D. Abbatt, K. L. Demerjian, and J. G. Anderson, J. Phys. Chem. **94** 4566 (1990).
[15] H. Mac Leod, C. Balestra, J. L. Jourdain, G. Laverdet, and G. Le Bras, Int J. Chem. Kinet. **22**, 1167 (1990).
[16] R. R. Baker, R. R. Baldwin, and R. W. Walker, Trans. Faraday Soc. **66**, 2812 (1970).
[17] R. R. Baldwin and R. W. Walker, J. Chem. Soc. Faraday Trans. 1, **75**, 140 (1979).
[18] R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **14**, 781 (1982).
[19] J. N. Bradley, W. Hack, K. Hoyermann, and H. Gg. Wagner, J. Chem. Soc. Faraday Trans. 1, **69**, 1889 (1973).
[20] F. P. Tully, A. R. Ravishankara, and K. Carr, Int. J. Chem. Kinet. **15**, 1111 (1983).
[21] V. Schmidt, G. Y. Zhu, K. H. Becker, and E. H. Fink, Ber. Bunsenges Phys. Chem. **89**, 321 (1985).
[22] A. Schiffman, D. D. Nelson, Jr., M. S. Robinson, and D. J. Nesbitt, J. Phys. Chem. **95**, 2629 (1991).
[23] D. L. Baulch, R. J. B. Craven, M. Din, D. D. Drysdale, S. Grant, D. J. Richardson, A. Walker, and G. Watling, J. Chem. Soc. Faraday Trans. 1, **79**, 689 (1983).
[24] E. O. Edney, T. E. Kleindienst, and E. W. Corse, Int. J. Chem. Kinet. **18**, 1355 (1986).

$HO + CO \rightarrow H + CO_2$ (1)
$HO + CO + M \rightarrow HOCO + M$ (2)

104.3 kJ·mol^{-1}
129 kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2$)

molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Rate Coefficients			
1.3×10^{-13}	298	Forster *et al.*, 1995[1]	(a)
4.1×10^{-33} [He]	298		
9.7×10^{-13}	298		
$1.8\times10^{-12}\exp(-2720/T) + 1.6\times10^{-13}\exp(-60/T)$	90–3000	Fulle *et al.*, 1996[2]	(b)
$2.0\times10^{-32}(T/300)^{-2.7}\exp(-490/T)\}$ [He]	90–3000		
$1.8\times10^{-11}\exp(-1850/T) + 1.5\times10^{-12}\exp(-130/T)$	90–3000		
and Evaluations			
$1.3\times10^{-13}[1 + 0.6\ P/\text{bar}]$	200–300	IUPAC, 1992[3]	(c)
$1.5\times10^{-13}[1 + 0.6\ P/\text{bar}]$	200–300	NASA, 1994[4]	(c)

Comments

(a) Laser flash photolysis experiments up to 150 bar of the bath gas He. Detection of HO radicals was by saturated LIF. The pressure dependence of k_1 and k_2 were represented by $k_1=k_{01}\{1-[x/(x+1)]F_c^{[1+(\log x)^2]^{-1}}\}$ and $k_2=k_{02}\{(1+y)/(1+x)\}F_c^{[1+(\log x)^2]^{-1}}$ with $x=k_{02}/(k_{\infty2}-k_{01})$, $y=k_{01}/(k_{\infty2}-k_{01})$ and $F_c(298\ K)=0.69$.

(b) Laser flash photolysis experiments over the range 80–900 K between 1 and 700 bar of the bath gas He. Detection of HO radicals was by saturated LIF. The data representation was consistent with statistical unimolecular rate theory in the form of comment (a), with $F_c=0.84$ at 100 K, 0.77 at 200 K, 0.73 at 250 K, and 0.69 at 300 K. Rate data for other bath gases will have to be analyzed by analogy to the He data, leading to different k_{02} and F_c values. The reaction enthalpy for reaction (2) was derived from experiments between 600 and 900 K.

(c) Weighted average of earlier data in $M=N_2$ at pressures below 1 bar. These experiments all require reanalysis with respect to the partitioning of k into k_1 and k_2 and the respective pressure dependences which, at temperatures near 200 K, are marked at pressures far below 1 bar.

Preferred Values

$k=1.3\times10^{-13}\,[1+(0.6\ P/\text{bar})(300/T)^{1.0}]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K and the pressure range 0–1 bar of N_2 or air.

Reliability

$\Delta\log k=\pm0.1$ at 298 K.

$\Delta\log k=\pm0.2$ over the temperature range 200–300 K.

Comments on Preferred Values

The preferred values at 298 K are only slightly changed from previous evaluations. However, the partitioning of the product channels between reactions (1) and (2) is included on the basis of the studies of Forster *et al.*[1] and Fulle *et al.*[2] Also, marked changes with decreasing temperature are accounted for, consistent with the recent experiments.[2]

References

[1] R. Forster, M. Frost, D. Fulle, H. F. Hamann, H. Hippler, A. Schlepegrell, and J. Troe, J. Chem. Phys. **103**, 2949 (1995).

[2] D. Fulle, H. F. Hamann, H. Hippler, and J. Troe, J. Chem. Phys. **105**, 983, 1001 (1996).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

$HO + HCHO \rightarrow H_2O + HCO$ (1)

$\rightarrow H + HCOOH$ (2)

$\Delta H^\circ(1) = -130.7\ \text{kJ}\cdot\text{mol}^{-1}$
$\Delta H^\circ(2) = -91.5\ \text{kJ}\cdot\text{mol}^{-1}$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comment
Absolute Rate Coefficients			
$(1.94 \pm 0.30) \times 10^{-11}$	1205±16	Bott and Cohen, 1991[1]	(a)
Reviews and Evaluations			
$8.8 \times 10^{-12} \exp(25/T)$	240–300	IUPAC, 1992[2]	(b)
$1.20 \times 10^{-14}\ T \exp(287/T)$	228–1205	Atkinson, 1994[3]	(c)
1.0×10^{-11}	228–576	NASA, 1994[4]	(d)

Comments

(a) HO radicals generated from thermal decomposition of *t*-butyl hydroperoxide in a shock tube, with detection by resonance absorption at 309 nm.

(b) Derived from the absolute rate coefficients determined by Atkinson and Pitts,[5] Stief *et al.*,[6] Temps and Wagner,[7] Zabarnick *et al.*,[8] and Yetter *et al.*[9] and the relative rate coefficient of Niki *et al.*[10] These rate coefficients[5–10] were fitted to the three parameter equation $k = CT^2\ e^{-D/T}$, yielding $k = 1.69 \times 10^{-17}\ T^2 \times \exp(557/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 228–572 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, was centered at 265 K and was derived from the three parameter expression with $A = C\ e^2\ T^2$ and $B = D + 2T$.

(c) Derived from the absolute rate coefficients of Atkinson and Pitts,[5] Stief *et al.*,[6] Temps and Wagner,[7] Yetter *et al.*,[9] and Bott and Cohen[1] and the relative rate coefficient of Niki *et al.*[10] (for $^{13}CH_2O$), using the expression $k = CT \exp(-D/T)$.

(d) The 298 K rate coefficient was the average of the absolute rate coefficients determined by Atkinson and Pitts,[5] Stief *et al.*,[6] Temps and Wagner,[7] and Zabarnick *et al.*[8] The combined data set yielded no evidence for any temperature dependence of the rate coefficient.

Preferred Values

$k = 9.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.6 \times 10^{-12} \exp(20/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.
$k_1/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 150$ K.
$\Delta(k_1/k) = \pm 0.10$ at 298 K.

Comments on Preferred Values

The absolute rate coefficients of Atkinson and Pitts,[5] Stief *et al.*,[6] Temps and Wagner,[7] Yetter *et al.*,[9] and Bott and Cohen[1] and the relative rate coefficient of Niki *et al.*[10] (for formaldehyde-^{13}C) were fitted to the three parameter expressions $k = CT \exp(-D/T)$ and $k = CT^2 \exp(-D/T)$, resulting in

$$k = 8.24 \times 10^{-18}\ T^2 \exp(753/T)\ \text{cm}^3\ \text{molecule}^{-1}\text{s}^{-1}$$

and

$$k = 1.20 \times 10^{-14}\ T \exp(287/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 228–1205 K. The expression $k = CT \exp(-D/T)$ gave a better fit to the data, and the preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter expression with $A = C\ e\ T$ and $B = D + T$.

The product data of Temps and Wagner[7] and Niki *et al.*[10] and the kinetic/modeling results of Yetter *et al.*[9] show that at 298 K this reaction proceeds via pathway (1) to yield H_2O + HCO.

References

[1] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **23**, 1075 (1991).
[2] IUPAC Supplement IV, 1992 (see references in Introduction).
[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] R. Atkinson and J. N. Pitts, Jr., J. Chem. Phys. **68**, 3581 (1978).
[6] L. J. Stief, D. F. Nava, W. A. Payne, and J. V. Michael, J. Chem. Phys. 73 2254 (1980).
[7] F. Temps and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **88**, 41 (1984).
[8] S. Zabarnick, J. W. Fleming, and M. C. Lin, Int. J. Chem. Kinet. **20**, 11 (1988).
[9] R. A. Yetter, H. Rabitz, F. L. Dryer, R. G. Maki, and R. B. Klemm, Chem. Phys. **91**, 4088 (1989).
[10] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phy Chem. **88**, 5342 (1984).

HO + $CH_3CHO \rightarrow H_2O + CH_3CO$

[illegible] = −139.6 kJ·mol^{-1}

Rate coefficient data

[illegible] molecule^{-1} s^{-1}	Temp./K	Reference	Comments
[illegible] Rate Coefficients			
([illegible]±0.10)×10^{-11}	298±2	Scollard *et al.*, 1993[1]	(a)
[illegible] and Evaluations			
[illegible]×10^{-12} exp(310/*T*)	240–530	IUPAC, 1992[2]	(b)
[illegible]×10^{-12} exp(311/*T*)	244–528	Atkinson, 1994[3]	(b)
[illegible]×10^{-12} exp(250/*T*)	244–528	NASA, 1994[4]	(c)

Comments

(a) Relative rate method. HO radicals were generated from the photolysis of CH_3ONO in air, and the concentrations of CH_3CHO and ethane measured during the experiments by GC. The measured rate constant ratio was placed on an absolute basis by use of *k*(HO + ethene) = 8.52×10^{-12} cm^3 molecule^{-1} s^{-1}.[5]

(b) Derived from the absolute rate coefficient data of Atkinson and Pitts[6] and Michael *et al.*,[7] and the relative rate coefficient of Niki *et al.*[8] at 298 K. The data of Semmes *et al.*[9] were not used in the evaluation because of their reported difficulties[9] in determining the acetaldehyde concentration.

(c) The 298 K rate coefficient was based upon the rate coefficient data of Morris *et al.*,[10] Niki *et al.*,[8] Atkinson and Pitts,[6] Kerr and Sheppard,[11] Semmes *et al.*,[9] and Michael *et al.*[7] The temperature dependence was the average of those measured by Atkinson and Pitts,[6] Semmes *et al.*,[9] and Michael *et al.*[7]

Preferred Values

$k = 1.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.6\times10^{-12}$ exp(310/*T*) cm^3 molecule^{-1} s^{-1} over the temperature range 240–530 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values were obtained from a least-squares analysis of the absolute rate coefficient data of Atkinson and Pitts[6] and Michael *et al.*,[7] and the relative rate coefficient of Niki *et al.*[8] at 298 K. The absolute and relative rate data of Morris *et al.*,[10] Cox *et al.*,[12] Kerr and Sheppard,[11] Balestra-Garcia *et al.*,[13] and Scollard *et al.*[1] are in agreement with the preferred 298 K value. The data of Semmes *et al.*,[9] which are lower than the preferred values by up to ~25%, were not used in the evaluation because of their reported difficulties in accurately determining the acetaldehyde concentrations.

While the absolute rate coefficients measured by Dóbé *et al.*[14] for CH_3CHO are in good agreement with the preferred values, their measured rate coefficients for the reactions of the HO radical with the higher aldehydes $(CH_3)_2CHCHO$ and $(CH_3)_3CCHO$ are significantly higher, by factors of ~1.5–2.3, than the rate coefficients of Kerr and Sheppard[11] and Semmes *et al.*[9] (which are in good agreement). Accordingly, the rate coefficient data of Dóbé *et al.*[14] have not been used in the evaluation.

References

[1] D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, J. Phys. Chem. **97**, 4683 (1993).

[2] IUPAC Supplement IV, 1992 (see references in Introduction).

[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

[5] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 1**, 1 (1989).

[6] R. Atkinson and J. N. Pitts, Jr., J. Chem. Phys. **68**, 3581 (1978).

[7] J. V. Michael, D. G. Keil, and R. B. Klemm, J. Chem. Phys. **83**, 1630 (1985).

[8] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **82**, 132 (1978).

[9] D. H. Semmes, A. R. Ravishankara, C. A. Gump-Perkins, and P. H. Wine, Int. J. Chem. Kinet. **17**, 303 (1985).

[10] E. D. Morris, Jr., D. H. Stedman, and H. Niki, J. Am. Chem. Soc. **93**, 3570 (1971).

[11] J. A. Kerr and D. W. Sheppard, Environ. Sci. Technol. **15**, 960 (1981).

[12] R. A. Cox, R. G. Derwent, P. M. Holt, and J. A. Kerr, J. Chem. Soc. Faraday Trans. 1, **72**, 2061 (1976).

[13] C. Balestra-Garcia, G. Le Bras, and H. Mac Leod, J. Phys. Chem. **96**, 3312 (1992).

[14] S. Dóbé, L. A. Khachatryan, and T. Bérces, Ber. Bunsenges. Phys. Chem. **93**, 847 (1989).

HO + $C_2H_5CHO \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=2.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.

Comments on Preferred Values

The preferred rate coefficient is derived from the mean of the absolute rate coefficient of Semmes *et al.*[1] and the relative rate coefficients of Niki *et al.*[2] and Kerr and Sheppard[3] and is identical to our previous evaluation, IUPAC, 1992.[4] The upper limit to the rate coefficient obtained by Kerr and Stocker[5] is consistent with the preferred value. The relative rate coefficient of Audley *et al.*[6] was not used in the evaluation, due to questions concerning the applicability of the experimental technique used.[1,7] The rate coefficient derived by Kaiser[8] at 553 K relative to those for ethene, propene and *trans*-2-butene of $\lesssim2.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, though of only semi-quantitative value, suggests a zero or close t zero temperature dependence, as expected by analogy with HCHO and CH_3CHO. The major reaction channel i expected[7] to be H-atom abstraction from the -CHO group t form $H_2O + C_2H_5CO$.

References

[1] D. H. Semmes, A. R. Ravishankara, C. A. Gump-Perkins, and P. H. Wi Int. J. Chem. Kinet. **17**, 303 (1985).

[2] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phy Chem. **82**, 132 (1978).

[3] J. A. Kerr and D. W. Sheppard, Environ. Sci. Technol. **15**, 960 (1981).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

[5] J. A. Kerr and D. W. Stocker, J. Photochem. **28**, 475 (1985).

[6] G. J. Audley, D. L. Baulch, and I. M. Campbell, J. Chem. Soc. Farada Trans. 1, **77**, 2541 (1981).

[7] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 1**, 1 (1989).

[8] E. W. Kaiser, Int. J. Chem. Kinet. **15**, 997 (1983).

HO + $(CHO)_2 \rightarrow H_2O$ + CHOCO

No new data have been published since our last evaluation.

Preferred Values

$k=1.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

Comments on Preferred Values

The preferred rate coefficient is based on the study of Plum *et al.*,[1] with increased uncertainty limits, and is identical to our previous evaluation, IUPAC, 1992.[2] The rate coefficient at 298 K is similar to those for other aldehydes. A close to zero temperature dependence is expected at around 298 K. The reaction is assumed to proceed via overall H-atom abstraction to yield H_2O + HC(O)CO. Niki *et al.*[3] showed from a study of the Cl atom-initiated reaction of glyoxal that at 298 K and 700 Torr total pressure the HC(O)CO radical reacts by the pathways,

$$HC(O)CO \rightarrow HCO + CO \quad (a)$$

$$HC(O)CO + O_2 \rightarrow HC(O)C(O)OO \quad (b)$$

$$HC(O)CO + O_2 \rightarrow 2CO + HO_2 \quad (c)$$

with $k_b \sim k_c$ and $k_a/k_b=3.5\times10^{18}$ molecule cm^{-3}.

References

[1] C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., Environ. Sci. Technol. **17**, 479 (1983).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **17**, 547 (1985).

$HO + HOCH_2CHO \rightarrow H_2O + HOCH_2CO$ (1)
$\rightarrow H_2O + HOCHCHO$ (2)

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2$)

$k=1.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k=0.80$ at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(k_1/k)=\pm0.10$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is taken from the study of Niki *et al.*,[1] with the error limits increased accordingly, and is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] H. Niki, P. D. Maker, C. M. Savage, and M. D. Hurley, J. Phys. Chem. **91**, 2174 (1987).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CH_3COCHO \rightarrow H_2O + CH_3COCO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.4\times10^{-13}\exp[(830\pm300)/T]$	273–333	Tyndall *et al.*, 1995[1]	(a)
$(1.32\pm0.30)\times10^{-11}$	298		
Reviews and Evaluations			
1.7×10^{-11}	298	IUPAC, 1992[2]	(b)

Comments

(a) Discharge flow system with LIF detection of HO radicals.
(b) Based on the relative rate coefficient of Plum *et al.*[3]

Preferred Values

$k=1.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is an average of the relative rate coefficient of Plum *et al.*[3] and the absolute rate coefficient of Tyndall *et al.*[1] The absolute rate coefficient measured by Kleindienst *et al.*[4] may have been low due to the presence of significant levels of low reactivity impurities in the methylglyoxal. The data of Tyndall *et al.*[1] indicate a significant negative temperature dependence; while no recommendation is made concerning the magnitude of the temperature dependence for this reaction a negative temperature dependence is expected at around room temperature (see, for example, the $HO + CH_3CHO$ reaction in this evaluation). The reaction is assumed to proceed via H-atom abstraction to form $H_2O + CH_3COCO$. Green *et al.*[5] have shown that the dominant fate of this CH_3COCO radical under atmospheric conditions is decomposition to form $CH_3CO + CO$.

References

[1] G. S. Tyndall, T. A. Staffelbach, J. J. Orlando, and J. G. Calvert, Int. J. Chem. Kinet. **27**, 1009 (1995).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., Environ. Sci. Technol. **17**, 479 (1983).
[4] T. E. Kleindienst, G. W. Harris, and J. N. Pitts, Jr., Environ. Sci. Technol. **16**, 844 (1982).
[5] M. Green, G. Yarwood, and H. Niki, Int. J. Chem. Kinet. **22**, 689 (1990).

$HO + CH_3COCH_3 \rightarrow H_2O + CH_3COCH_2$

$\Delta H° = -87.8\ kJ \cdot mol^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.80 \pm 1.32) \times 10^{-12}$	1217	Bott and Cohen, 1991[1]	(a)
Reviews and Evaluations			
$1.7 \times 10^{-12} \exp(-600/T)$	240–440	IUPAC, 1989[2], 1992[3]	(b)
$5.34 \times 10^{-18}\ T^2 \exp(-230/T)$	240–1217	Atkinson, 1994[4]	(c)

Comments

(a) HO radicals were generated by the thermal decomposition of *t*-butyl hydroperoxide in a shock tube, and monitored by resonance absorption at 309 nm.

(b) Derived from the absolute rate coefficient study of Wallington and Kurylo.[5]

(c) Derived from the absolute rate coefficients of Wallington and Kurylo[5] and Bott and Cohen[1] and the relative rate constant of Kerr and Stocker,[6] using the expression $k = CT^2 \exp(-D/T)$.

Preferred Values

$k = 2.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.8 \times 10^{-12} \exp(-760/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values are based on the absolute rate coefficient data of Wallington and Kurylo[5] and Bott and Cohen[1] and the relative rate constant of Kerr and Stocker.[6] These data[1,5,6] have been fitted to the three-parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 5.34 \times 10^{-18}\ T^2 \times \exp(-230/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–1217 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = C\ e^2\ T^2$ and $B = D + 2T$. The 298 K rate coefficient is similar to that for the HO radical reaction with ethane (this evaluation) and the present recommendation for the temperature dependence is more similar to that for ethane than was the previous IUPAC (1989, 1992) evaluation.[2,3]

References

[1] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **23**, 1017 (1991).
[2] IUPAC, Supplement III, 1989 (see references in Introduction).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[5] T. J. Wallington and M. J. Kurylo, J. Phys. Chem. **91**, 5050 (1987).
[6] J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).

$HO + CH_3OH \rightarrow H_2O + CH_2OH \quad (1)$
$\rightarrow H_2O + CH_3O \quad (2)$

$\Delta H°(1) = -88.5\ kJ \cdot mol^{-1}$
$\Delta H°(2) = -61.9\ kJ \cdot mol^{-1}$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comment
Absolute Rate Coefficients			
$(8.64 \pm 1.30) \times 10^{-12}$	1205 ± 16	Bott and Cohen, 1991[1]	(a)
Reviews and Evaluations			
$3.3 \times 10^{-12} \exp(-380/T)$	240–300	IUPAC, 1992[2]	(b)
$6.01 \times 10^{-18}\ T^2 \exp(170/T)$	240–1205	Atkinson, 1994[3]	(c)
$6.7 \times 10^{-12} \exp(-600/T)$	240–400	NASA, 1994[4]	(d)

Comments

(a) HO radicals were generated from the thermal decomposition of *t*-butyl hydroperoxide in a shock tube, and monitored by resonance absorption at 309 nm.

(b) Derived from the absolute rate coefficients of Overend and Paraskevopoulos,[5] Ravishankara and Davis,[6] Wallington and Kurylo,[7] McCaully *et al.*,[8] Hess and Tully,[9] and Nelson *et al.*[10] and the relative rate coefficient of Tuazon *et al.*[11] These data[5–11] were fitted to the three parameter expression $k=CT^2\exp(-D/T)$, resulting in $k=6.37\times10^{-18}\,T^2\times\exp(150/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–866 K. The Arrhenius expression is centered at 265 K and was derived from the three parameter expression with $A=C\,e^2\,T^2$ and $B=D+2T$.

(c) Derived from the absolute rate coefficients of Overend and Paraskevopoulos,[5] Ravishankara and Davis,[6] Wallington and Kurylo,[7] McCaully *et al.*,[8] Hess and Tully,[9] Nelson *et al.*,[10] and Bott and Cohen[1] and the relative rate coefficient of Tuazon *et al.*,[11] using the three parameter equation $k=CT^2\exp(-D/T)$.

(d) The 298 K rate coefficient was the average of the absolute rate coefficients of Overend and Paraskevopoulos,[5] Ravishankara and Davis,[6] Hägele *et al.*,[12] Meier *et al.*,[13] Greenhill and O'Grady,[14] Wallington and Kurylo,[7] and Hess and Tully.[9] The temperature dependence was derived from those reported by Greenhill and O'Grady[14] and Wallington and Kurylo.[7]

Preferred Values

$k=9.3\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=3.1\times10^{-12}\exp(-360/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.
$k_2/k=0.15$ at 298 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.
$\Delta(E/R)=\pm200$ K.
$\Delta k_2/k=\pm0.10$ at 298 K.

Comments on Preferred Values

The preferred rate coefficient is obtained by fitting the absolute rate coefficients of Overend and Paraskevopoulos,[5] Ravishankara and Davis,[6] Wallington and Kurylo,[7] McCaully *et al.*,[8] Hess and Tully,[9] Nelson *et al.*,[10] and Bott and Cohen[1] and the relative rate coefficient of Tuazon *et al.*[11] to the three parameter expression $k=CT^2\exp(-D/T)$. This results in $k=6.01\times10^{-18}\,T^2\exp(170/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–1205 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$, is centered at 265 K, and is derived from the three parameter equation with $A=C\,e^2\,T^2$ and $B=D+2T$. The kinetic[8] and product[12,13] studies show that the reaction proceeds mainly by step (1) at room temperature, as expected from the thermochemistry of the reaction steps (1) and (2).

References

[1] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **23**, 1075 (1991).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] R. Overend and G. Paraskevopoulos, J. Phys. Chem. **82**, 1329 (1978).
[6] A. R. Ravishankara and D. D. Davis, J. Phys. Chem. **82**, 2852 (1978).
[7] T. J. Wallington and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 1015 (1987).
[8] J. A. McCaulley, N. Kelly, M. F. Golde, and F. Kaufman, J. Phys. Chem. **93**, 1014 (1989).
[9] W. P. Hess and F. P. Tully, J. Phys. Chem. **93**, 1944 (1989).
[10] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).
[11] E. C. Tuazon, W. P. L. Carter, R. Atkinson, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **15**, 619 (1983).
[12] J. Hägele, K. Lorenz, D. Rhäsa, and R. Zellner, Ber. Bunsenges. Phys. Chem. **87**, 1023 (1983).
[13] U. Meier, H. H. Grotheer, and Th. Just, Chem. Phys. Lett. **106**, 97 (1984).
[14] P. G. Greenhill and B. V. O'Grady, Aust. J. Chem. **39**, 1775 (1986).

$$\begin{aligned} \mathrm{HO} + \mathrm{C_2H_5OH} &\rightarrow \mathrm{H_2O} + \mathrm{CH_2CH_2OH} \quad (1)\\ &\rightarrow \mathrm{H_2O} + \mathrm{CH_3CHOH} \quad (2)\\ &\rightarrow \mathrm{H_2O} + \mathrm{CH_3CH_2O} \quad (3) \end{aligned}$$

$\Delta H^\circ(1)=-80$ kJ·mol^{-1}
$\Delta H^\circ(2)=-109.9$ kJ·mol^{-1}
$\Delta H^\circ(3)=-63.5$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2+k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_2+k_3=(8.80\pm1.32)\times10^{-12}$	1204±16	Bott and Cohen, 1991[1]	(a)
Reviews and Evaluations			
$4.1\times10^{-12}\exp(-70/T)$	270–340	IUPAC, 1992[2]	(b)
$6.18\times10^{-18}\,T^2\exp(532/T)$	293–599	Atkinson, 1994[3]	(c)
$7.0\times10^{-12}\exp(-235/T)$	240–600	NASA, 1994[4]	(d)

Comments

(a) HO radicals were generated by the thermal desorption of *t*-butyl hydroperoxide in a shock tube, with detection by resonance absorption at 309 nm. The measured rate coefficient corresponds to (k_2+k_3) because of the rapid thermal decomposition of the CH_2CH_2OH radical formed in reaction channel (1) (this is the same radical as formed from the addition of HO radicals to ethene).

(b) Derived from the HO^{18} radical and (for temperatures <500 K) the HO^{16} radical rate coefficients of Hess and Tully.[5] These data[5] were fitted to the three parameter expression $k=CT^2\exp(-D/T)$, resulting in $k=6.18\times10^{-18}T^2\times\exp(532/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 293–599 K. The Arrhenius expression, $k=A\exp(-B/T)$, was centered at 300 K and was derived from the three parameter expression with $A=C\,e^2\,T^2$ and $B=D+2T$.

(c) Derived from the HO^{18} rate coefficients and the <500 K HO^{16} rate coefficients measured by Hess and Tully,[5] using the three parameter equation $k=CT^2\exp(-D/T)$. This expression is expected to be the overall rate constant $k=k_1+k_2+k_3$.

(d) The 298 K rate coefficient was the average of the room temperature rate coefficients of Campbell *et al.*,[6] Overend and Paraskevopoulos,[7] Ravishankara and Davis,[8] Cox and Goldstone,[9] Kerr and Stocker,[10] Wallington and Kurylo,[11] and Hess and Tully.[5] The temperature dependence was obtained by averaging the temperature dependencies of the rate coefficients reported by Wallington and Kurylo[11] and Hess and Tully.[5]

Preferred Values

$k=3.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=4.1\times10^{-12}\exp(-70/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.
$k_1/k=0.05$ at 298 K.
$k_3/k=0.05$ at 298 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.
$\Delta(E/R)=\pm200$ K.
$\Delta k_1/k=^{+0.10}_{-0.05}$ at 298 K.
$\Delta k_3/k=^{+0.10}_{-0.05}$ at 298 K.

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.[2] There is substantial scatter in the room temperature rate coefficients measured to date. The most definite study to date is that of Hess and Tully.[5] The preferred rate coefficient is derived from fitting the HO^{18} and (for temperatures <500 K) the HO^{16} rate coefficient data of Hess and Tully[5] to the three parameter expression $k=CT^2\times\exp(-D/T)$. This results in $k=6.18\times10^{-18}T^2\exp(532/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 293–599 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$ is centered at 300 K and is derived from this three parameter expression with $A=C\,e^2\,T^2$ and $B=D+2T$. The rate coefficients calculated from the preferred Arrhenius expression are ~10% higher than the lowest temperature rate coefficients reported by Greenhill and O'Grady[12] (at 255 K) and Wallington and Kurylo[11] (at 240 K). The preferred 298 K rate coefficient is in good agreement with the absolute and relative rate coefficients of Nelson *et al.*[13] The rate coefficient measured by Bott and Cohen[1] at 1204 K, and ascribed to (k_2+k_3), is consistent with the value of $(k_1+k_2+k_3)$ calculated from the recommended three parameter expression and with the rate coefficient k_1 at 1204 K estimated using the procedure of Atkinson.[14]

Meier *et al.*[15] determined that at room temperature the reaction proceeds mainly (75±15%) via formation of the CH_3CHOH radical, consistent with the expected thermochemistry of the reaction steps. The kinetic data of Hess and Tully[5] for the reactions of the HO^{16} and HO^{18} radicals with ethanol indicate that channel (1) accounts for ~15% of the overall reaction at 600 K, in agreement with the calculated value of ~20% from the estimation procedure of Atkinson.[14] This agreement allows a rate coefficient ratio of $k_1/k=0.05$ at 298 K to be estimated. Assuming that H-atom abstraction from the -OH group in ethanol [channel (3)] has a similar rate coefficient to the analogous channel for methanol (this evaluation) allows $k_3/k=0.05$ at 298 K to be estimated. The resulting value of $k_2/k=0.90$ at 298 K is just consistent with the product data of Meier *et al.*[15]

References

[1] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **23**, 1075 (1991).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] W. P. Hess and F. P. Tully, Chem. Phys. Lett. **152**, 183 (1988).
[6] I. M. Campbell, D. F. McLaughlin, and B. J. Handy, Chem. Phys. Lett. **38**, 362 (1976).
[7] R. Overend and G. Paraskevopoulos, J. Phys. Chem. **82**, 1329 (1978).
[8] A. R. Ravishankara and D. D. Davis, J. Phys. Chem. **82**, 2852 (1978).
[9] R. A. Cox and A. Goldstone, *Proceedings of the 2nd European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants* (Reidel, Dordrecht, Holland, 1982), pp. 112–119.
[10] J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).
[11] T. J. Wallington and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 1015 (1987).
[12] P. G. Greenhill and B. V. O'Grady, Aust. J. Chem. **39**, 1775 (1986).
[13] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).
[14] R. Atkinson, Int. J. Chem. Kinet. **19**, 799 (1987).
[15] U. Meier, H. H. Grotheer, G. Riekert, and Th. Just, Chem. Phys. Lett. **115**, 221 (1985).

HO + n-C_3H_7OH → products

No new data have been published since our last evaluation.

Preferred Values

$k=5.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

Comments on Preferred Values

The experimental technique of Campbell *et al.*[1] was possibly prone to unrecognized problems,[2] and hence this rate coefficient was not used in deriving the preferred values. The 298 K value is the mean of the absolute rate coefficients of Overend and Paraskevopoulos,[3] Wallington and Kurylo,[4] and Nelson *et al.*[5] and the relative rate coefficient of Nelson *et al.*[5] The preferred values are identical to our previous evaluation, IUPAC, 1992.[6]

References

[1] I. M. Campbell, D. F. McLaughlin, and B. J. Handy, Chem. Phys. Lett. **38**, 362 (1976).

[2] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 1**, 1 (1989).

[3] R. Overend and G. Paraskevopoulos, J. Phys. Chem. **82**, 1329 (1976).

[4] T. J. Wallington and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 1015 (1987).

[5] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + i-C_3H_7OH → $H_2O + (CH_3)_2CHO$ (1)
→ $H_2O + CH_3C(OH)CH_3$ (2)
→ $H_2O + CH_3CH(OH)CH_2$ (3)

$\Delta H^\circ(1) = -60.9$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2+k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.044\times10^{-17}\,T^{1.86}\exp(736/T)$	293–587	Dunlop and Tully, 1993[1]	(a)
$(5.10\pm0.21)\times10^{-12}$	293		
Reviews and Evaluations			
5.7×10^{-12}	240–440	IUPAC, 1992[2]	(b)
$4.06\times10^{-18}\,T^2\exp(788/T)$	293–587	Atkinson, 1994[3]	(c)

Comments

(a) Pulsed laser photolysis system with LIF detection of HO radicals. The reactions of HO^{16} radicals were studied over the temperature range 293–745 K and the reactions of HO^{18} radicals were studied at 548 K and 587 K. Non-exponential decays of HO^{16} radicals were observed over the temperature range 504–600 K[1] and, while exponential HO^{16} radical decays were observed above 600 K,[1] the rate coefficients were significantly lower than expected from extrapolation of the lower temperature data.[1] These observations are consistent with thermal decomposition of the $CH_3CH(OH)CH_2$ radical formed in reaction channel (3) [the same radical as formed from HO radical addition to propene] at temperatures $\gtrsim$500 K. Hence using HO^{16} radicals, values of $k_1+k_2+k_3$ were measured at temperatures $\leq$500 K and k_1+k_2 at temperatures $\gtrsim$600 K. No regeneration of HO^{18} radicals from thermal decomposition of the $CH_3CH(^{16}OH)CH_2$ radical can occur, and hence the measured HO^{18} rate coefficients are those for $(k_1+k_2+k_3)$.

(b) The preferred 298 K rate coefficient was the average of the room temperature absolute rate coefficients of Overend and Paraskevopoulos,[4] Wallington and Kurylo,[5] and Nelson *et al.*[6] and the relative rate coefficient of Nelson *et al.*[6] A zero temperature dependence was used, consistent with the data of Wallington and Kurylo.[5]

(c) Derived from the HO^{18} radical and (for temperatures $\leq$502 K) HO^{16} radical rate coefficients of Dunlop and Tully.[1] These rate coefficients[1] were fitted to the three parameter expression $k=CT^2\exp(-D/T)$.

Preferred Values

$k=5.1\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=2.7\times10^{-12}\exp(190/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred rate coefficients are derived from the data obtained by Dunlop and Tully.[1] The HO^{18} rate coefficients at 548 K and 587 K and the HO^{16} rate coefficients at $\leqslant 502$ K were fitted to the three parameter expression $k = CT^2 \times \exp(-D/T)$, resulting in $k = 4.06 \times 10^{-18}\ T^2 \exp(788/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 293–587 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three parameter expression with $A = C\ e^2\ T^2$ and $B = D + 2T$. The preferred rate coefficients are ~10% lower than those of Wallington and Kurylo[5] over the temperature range 270–340 K.

References

[1] J. R. Dunlop and F. P. Tully, J. Phys. Chem. **97**, 6457 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[4] R. Overend and G. Paraskevopoulos, J. Phys. Chem. **82**, 1329 (1978).

[5] T. J. Wallington and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 1015 (198

[6] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

$HO + CH_3OCH_3 \rightarrow H_2O + CH_3OCH_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.29 \times 10^{-11} \exp[-(388 \pm 151)/T]$	299–424	Perry, Atkinson, and Pitts, 1977[1]	(a)
$(3.50 \pm 0.35) \times 10^{-12}$	298.9		
$1.04 \times 10^{-11} \exp[-(372 \pm 34)/T]$	295–442	Tully and Droege, 1987[2]	(b)
$(2.95 \pm 0.12) \times 10^{-12}$	295		
$6.7 \times 10^{-12} \exp[-(300 \pm 70)/T]$	240–440	Wallington *et al.*, 1988[3]	(a)
$(2.49 \pm 0.22) \times 10^{-12}$	296		
$(2.35 \pm 0.24) \times 10^{-12}$	298±2	Nelson *et al.*, 1990[4]	(c)
Relative Rate Coefficients			
$(2.30 \pm 0.23) \times 10^{-12}$	295±3	Wallington *et al.*, 1989[5]	(d)
$(3.19 \pm 0.70) \times 10^{-12}$	298±2	Nelson *et al.*, 1990[4]	(e)
Reviews and Evaluations			
$1.04 \times 10^{-11} \exp(-372/T)$	295–442	Atkinson, 1994[6]	(f)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO radicals.

(b) Laser photolysis system with LIF detection of HO radicals.

(c) Pulsed radiolysis system with resonance absorption detection of HO radicals.

(d) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at atmospheric pressure. Concentrations of dimethyl ether and n-butane measured during the experiment by GC and the rate coefficient ratio of $k(CH_3OCH_3)/k(n\text{-butane}) = 0.918 \pm 0.090$ placed on an absolute basis by using $k(n\text{-butane}) = 2.50 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[6]

(e) Relative rate method. HO radicals generated by the photolysis of CH_3ONO-NO-air mixtures at atmospheric pressure. Concentrations of dimethyl ether and cyclohexane measured during the experiments by GC, and the rate coefficient ratio $k(CH_3OCH_3)/k(\text{cyclohexane})$ placed on an absolute basis by use of $k(\text{cyclohexane}) = 7.49 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[6]

(f) Based on the absolute rate coefficient data of Tully and Droege.[2]

Preferred Values

$k = 2.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.0 \times 10^{-11} \exp(-370/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–450 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The reported room temperature absolute[1–4] and relative[4,5] rate coefficients exhibit appreciable scatter, covering a range of a factor of 1.5. The measured temperature dependencies[1–3] are in good agreement. The preferred values are based on the absolute rate coefficient study of Tully and the data of which are between those of the other absolute temperature-dependent studies of Perry *et al.*[1] and Wallington *et al.*[3]

References

[1] R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. **67**, 611

[2] F. P. Tully and A. T. Droege, Int. J. Chem. Kinet. **19**, 251 (1987).

[3] T. J. Wallington, R. Liu, P. Dagaut, and M. J. Kurylo, Int. J. Chem. Kinet. **20**, 41 (1988).

[4] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

[5] T. J. Wallington, J. M. Andino, L. M. Skewes, W. O. Siegl, and S. M. Japar, Int. J. Chem. Kinet. **21**, 993 (1989).

[6] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

HO + $CH_3COCH_2OH \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k = 3.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

Based on the sole study of Dagaut *et al.*,[1] with expanded uncertainty limits. The preferred value is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] P. Dagaut, R. Liu, T. J. Wallington, and M. J. Kurylo, J. Phys. Chem. **93**, 7838 (1989).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + $CH_3OOH \rightarrow H_2O + CH_2OOH$ (1)
$\rightarrow H_2O + CH_3OO$ (2)

$\Delta H^\circ(1) = -140$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.9 \times 10^{-12} \exp(190/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–430 K.

$k_1/k = 0.35$ over the temperature range 220–430 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 150$ K.

$\Delta(k_1/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred values are those of Vaghjiani and Ravishankara.[1] The preferred branching ratio, also taken from the absolute rate coefficient study of Vaghjiani and Ravishankara,[1] is in good agreement with the earlier measurement of Niki *et al.*[2] The preferred values are identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] G. L. Vaghjiani and A. R. Ravishankara, J. Phys. Chem. **93**, 1948 (1989).

[2] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **87**, 2190 (1983).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + HCOOH → products

No new data have been published since our last evaluation.

Preferred Values

$k=4.5\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–450 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.
$\Delta(E/R)=\pm250$ K.

Comments on Preferred Values

A major problem with the determination of the rate coefficient for this reaction concerns the ready dimerization of HCOOH. The studies of Wine *et al.*,[1] Jolly *et al.*,[2] and Singleton *et al.*[3] monitored formic acid in the experimental systems used by UV absorption spectroscopy. The data from these studies[1-3] agree well, and are in reasonable agreement with the room temperature rate coefficient of Dagaut *et al.*[4] The data of Wine *et al.*[1] and Singleton *et al.*[3] show that the temperature dependence of the rate coefficient is zero within the experimental uncertainties. The average of the rate coefficient data of Wine *et al.*,[1] Jolly *et al.*,[2] and Singleton *et al.*[3] has been used to derive the preferred rate coefficient. The preferred values are identical to our previous evaluation, IUPAC, 1992.[5]

The studies of Wine *et al.*[1] and Jolly *et al.*[2] showed that H atoms are produced in this reaction, with a yield of 0.75 ±0.25.[1] Furthermore, Wine *et al.*[1] and Singleton *et al.* showed that within the experimental uncertainties the rate coefficient for the reaction of the HO radical with DCOOH is identical to that for HCOOH at 298 K. Also, the room temperature rate coefficients for the reactions of the DO radicals with HCOOD and DCOOD are significantly lower than those for the reactions of the HO radical with HCOOH and DCOOH.[3] This reaction then appears to proceed by

$$\begin{tikzcd} \mathrm{OH + HC(O)OH} \arrow[r] & \mathrm{H_2O + HCO_2} \arrow[d] \\ & \mathrm{H + CO_2} \end{tikzcd}$$

with overall abstraction of the H (or D) atom from the -OH (or -OD) group being the major pathway at room temperature.

References

[1] P. H. Wine, R. J. Astalos, and R. L. Mauldin, III, J. Phys. Chem. **89**, 2620 (1985).
[2] G. S. Jolly, D. J. McKenney, D. L. Singleton, G. Paraskevopoulos, and A. R. Bossard, J. Phys. Chem. **90**, 6557 (1986).
[3] D. L. Singleton, G. Paraskevopoulos, R. S. Irwin, G. S. Jolly, and D. J. McKenney, J. Am. Chem. Soc. **110**, 7786 (1988).
[4] P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, Int. J. Chem. Kinet. **20**, 331 (1988).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + CH_3COOH → products

No new data have been published since our last evaluation.

Preferred Values

$k=8\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

Comments on Preferred Values

At 298 K, the rate coefficients of Dagaut *et al.*[1] and Singleton *et al.*[2] are in reasonable agreement. However, at temperatures above 298 K, Dagaut *et al.*[1] observed the rate coefficient to increase with increasing temperature, while Singleton *et al.*[2] observed the rate coefficient to decrease in a non-Arrhenius manner with increasing temperature. At 400–440 K, the rate coefficients of Dagaut *et al.*[1] and Singleton *et al.*[2] disagree by a factor of 2.2.

The preferred 298 K rate coefficient is an average of the data of Dagaut *et al.*[1] and Singleton *et al.*[2] No recommendation is made regarding the temperature dependence. The preferred value is identical to our previous evaluation, IUPAC, 1992.[3] The rate coefficient data of Singleton *et al.*[3] for the reactions of the HO radical with CH_3COOH, CD_3COOH, and CD_3COOD indicate that at room temperature the major reaction channel involves overall H atom abstraction from the -OH bond:

$$HO + CH_3C(O)OH \rightarrow H_2O + CH_3CO_2$$

References

[1] P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, Int. J. Chem. Kinet. 20, 331 (1988).
[2] D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, J. Am. Chem. Soc. 111, 5248 (1989).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + $C_2H_5COOH \rightarrow$ products

Rate coefficient data

[illegible] molecule^{-1} s^{-1}	Temp./K	Reference	Comments
[illegible] Rate Coefficients			
[illegible] $\exp[-(120\pm30)/T]$	298–440	Dagaut *et al.*, 1988[1]	(a)
[illegible]$0.12)\times10^{-12}$	298		
[illegible]$0.05)\times10^{-12}$	298–445	Singleton, Paraskevopoulos, and Irwin, 1989[2]	(b)
[illegible]$0.35)\times10^{-12}$	298		
[illegible] and Evaluations			
[illegible]	298–445	Atkinson, 1994[3]	(c)

Comments

[illegible] Flash photolysis system with resonance fluorescence detection of HO radicals.

[illegible] Pulsed laser photolysis system with resonance absorption detection of HO radicals.

[illegible] Derived from an average of all of the rate coefficients of Dagaut *et al.*[1] and Singleton *et al.*[2] These data[1,2] indicate that the rate coefficient is independent of temperature over the range 298–445 K.

Preferred Values

$k = 1.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–450 K.

Reliability

$\Delta \log k = \pm0.2$ at 298 K.

$\Delta(E/R) = +300$ K.

Comments on Preferred Values

The rate coefficients measured by Dagaut *et al.*[1] and Singleton *et al.*[2] are in good agreement and indicate that the rate coefficient for this reaction is independent of temperature over the range 298–445 K. The preferred value is an average of all of the rate coefficients of Dagaut *et al.*[1] and Singleton *et al.*,[2] combined with a zero temperature dependence. The reaction is expected to proceed by H-atom abstraction from the C-H bonds of the -CH_3 group and the O-H bond of the -C(O)OH group.

References

[1] P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, Int. J. Chem. Kinet. **20**, 331 (1988).

[2] D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, J. Am. Chem. Soc. **111**, 5248 (1989).

[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

HO + $CH_3ONO_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k = 3.5\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.

$k = 1.0\times10^{-14}\exp(1060/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–400 K at 1 bar.

Reliability

$\Delta \log k = \pm0.10$ at 298 K (1 bar).

$\Delta(E/R) = \pm500$ K.

Comments on Preferred Values

At room temperature, the absolute and relative rate coefficients of Nielsen *et al.*[1] and Kerr and Stocker[2] measured at 1 bar pressure are in good agreement, but are an order of magnitude higher than the rate coefficient measured by Gaffney *et al.*[3] at 0.003–0.004 bar pressure. This may indicate that the rate coefficient is pressure dependent and hence that the reaction proceeds by H-atom abstraction and OH radical addition (and by ~90% OH radical addition at 298 K and 1 bar). This conclusion is supported by the observed negative temperature dependence.[1] The preferred 298 K rate coefficient is the average of the absolute and relative rate coefficients of Nielsen *et al.*[1] and Kerr and Stocker[2] (note that formation of CH_3ONO_2 in the photolysis of CH_3ONO-NO-air mixtures could have led to a low measured rate coefficient in the relative rate coefficient study of Nielsen *et al.*,[1] although the agreement of this relative rate coefficient[1] with the absolute rate coefficient of Nielsen *et al.*[1] and the relative rate coefficient of Kerr and Stocker[2] suggests that any such formation of CH_3ONO_2 was small). The temperature dependence is derived from the absolute rate coefficient data of Nielsen *et al.*,[1] and is applicable only at 1 bar pressure. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).
[2] J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).
[3] J. S. Gaffney, R. Fajer, G. I. Senum, and J. H. Lee, Int. J. Chem. Kinet. 18, 399 (1986).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + $C_2H_5ONO_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=4.9\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.
$k=4.4\times10^{-14}$ exp(720/T) cm^3 molecule^{-1} s^{-1} over the temperature range 290–380 K at 1 bar.

Reliability
$\Delta\log k=\pm0.15$ at 298 K (1 bar).
$\Delta(E/R)=\pm500$ K (1 bar).

Comments on Preferred Values

The absolute and relative rate coefficients of Kerr and Stocker[1] and Nielsen *et al.*[2] are in good agreement at room temperature. All three rate coefficients have been determined at ~1 bar pressure, and it is possible that the rate coefficient is pressure dependent at low total pressures. The preferred 298 K rate coefficient is the average of those determined by Kerr and Stocker[1] and Nielsen *et al.*[2] The preferred temperature dependence is that of Nielsen *et al.*[2] The preferred values are applicable to 1 bar pressure and are identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).
[2] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + n-$C_3H_7ONO_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=7.3\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–370 K (1 bar).

Reliability
$\Delta\log k=\pm0.15$ at 298 K (1 bar).
$\Delta(E/R)=\pm500$ K (1 bar).

Comments on Preferred Values

The absolute and relative rate coefficients of Kerr and Stocker,[1] Atkinson and Aschmann,[2] and Nielsen *et al.*[3] are in reasonable agreement at room temperature. All studies have been carried out at ~1 bar pressure. The reaction may proceed by H-atom abstraction and OH radical addition, and the rate coefficient may be pressure dependent at low total pressures. The preferred 298 K rate coefficient is the average of those measured by Kerr and Stocker,[1] Atkinson and Aschmann,[2] and Nielsen *et al.*[3] A zero temperature dependence is assumed, consistent with the data of Nielsen *et al.*[3] The preferred rate coefficients are applicable to 1 bar pressure, and are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).
[2] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **21**, 1123 (1989).
[3] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + i-$C_3H_7ONO_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=4.9\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.

Reliability

$\Delta\log k=\pm0.25$ at 298 K (1 bar).

Comments on Preferred Values

The study of Atkinson and Aschmann,[1] carried out in a 6400 liter reaction chamber, supersedes the earlier study of Atkinson *et al.*[2] carried out in a 50 liter chamber and in which wall losses were concluded (probably erroneously) to have occurred. The relative rate coefficients of Becker and Wirtz[3] and Atkinson and Aschmann[1] are in reasonable agreement. The preferred 298 K rate coefficient is the average of those of Becker and Wirtz[3] and Atkinson and Aschmann,[1] and is identical to our previous evaluation, IUPAC, 1992.[4] As for the other alkyl nitrates, this reaction may proceed by H-atom abstraction and OH radical addition, and the preferred rate coefficient is applicable to 1 bar pressure.

References

[1] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **21**, 1123 (1989).

[2] R. Atkinson, S. M. Aschmann, W. P. L. Carter, and A. M. Winer, Int. J. Chem. Kinet. **14**, 919 (1982).

[3] K. H. Becker and K. Wirtz, J. Atmos. Chem. **9**, 419 (1989).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CH_3CO_3NO_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=1.1\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=9.5\times10^{-13}\exp(-650/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–300 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm400$ K.

Comments on Preferred Values

The 298 preferred value is the average of the room temperature rate coefficients of Wallington *et al.*[1] and Tsalkani *et al.*,[2] both of which are consistent with the upper limit to the rate coefficient previously determined by Winer *et al.*[3] The temperature dependence is that reported by Wallington *et al.*[1] The preferred values are identical to our previous evaluation, IUPAC, 1992.[4] The reaction is expected to proceed via H-atom abstraction from the C-H bonds to yield $H_2O + CH_2CO_3NO_2$.

References

[1] T. J. Wallington, R. Atkinson, and A. M. Winer, Geophys. Res. Lett. **11**, 861 (1984).

[2] N. Tsalkani, A. Mellouki, G. Poulet, G. Toupance, and G. Le Bras, J. Atmos. Chem. 7, 409 (1988).

[3] A. M. Winer, A. C. Lloyd, K. R. Darnall, R. Atkinson, and J. N. Pitts, Jr., Chem. Phys. Lett. **51**, 221 (1977).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CH_3COCH_2ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$<4.4\times10^{-13}$	298±2	Zhu, Barnes, and Becker, 1991[1]	(a)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO-NO-N_2-O_2 mixtures at 1 bar pressure. Concentrations of $CH_3COCH_2ONO_2$ and n-butane were measured during the experiments by GC, and the rate constant ratio of $k(CH_3COCH_2ONO_2)/k(n\text{-butane}) < 0.17$ was placed on an absolute basis by use of a rate coefficient of $k(n\text{-butane})=2.54\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[2]

Preferred Values

$k<1\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

Based on the sole study of Zhu *et al.*,[1] but with a higher upper limit to reflect additional uncertainties.

References

[1] T. Zhu, I. Barnes, and K. H. Becker, J. Atmos. Chem. **13**, 301 (1991).

[2] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

HO + HCN → products

No new data have been published since our last evaluation.

Preferred Values

$k=3\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.
$k=1.2\times10^{-13}\exp(-400/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–440 K at 1 bar.

Reliability

$\Delta\log k=\pm0.5$ at 298 K.
$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The preferred values are those of Fritz *et al.*[1] with wider error limits. The rate coefficient increases with increasing pressure over this temperature range, and the rate coefficients cited are those extrapolated by Fritz *et al.*[1] to the high-pressure limit. The preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

The reaction proceeds by HO radical addition over this temperature range. At higher temperatures the available rate coefficient data indicate a direct abstraction reaction.[3]

References

[1] B. Fritz, K. Lorenz, W. Steinert, and R. Zellner, Oxid. Comm. **6**, 363 (1984).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 1**, 1 (1989).

HO + CH_3CN → products

No new data have been published since our last evaluation.

Preferred Values

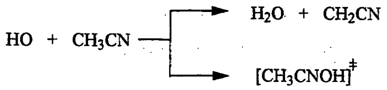
$k=2.2\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K (1 bar).
$k=8.1\times10^{-13}\exp(-1080/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–390 K (1 bar).

Reliability

$\Delta\log k=\pm0.15$ at 298 K.
$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is a unit-weighted average of the rate coefficients of Poulet *et al.*,[1] Kurylo and Knable,[2] and Hynes and Wine.[3] The temperature dependence is the mean of those determined by Kurylo and Knable[2] and Hynes and Wine.[3] The mechanism and products of this reaction are not understood at present. Hynes and Wine[3] observed no definitive evidence for a pressure dependence of the rate coefficient for the HO + CH_3CN reaction in N_2 or He diluent over the pressure range 46–700 Torr (N_2 diluent) or 30–630 Torr (He diluent). In the presence of O_2, the HO radical decays were nonexponential,[3] indicating regeneration of HO radicals. Combined with analogous data for the reactions of HO radicals with CD_3CN (for which the rate coefficient was pressure dependent over the pressure range 40–692 Torr of N_2 diluent)[3] and of DO radicals with CH_3CN and CD_3CN,[3] these data suggest that the initial HO radical reaction proceeds by H-atom abstraction from the -CH_3 group and HO radical addition to the -CN group.[3]



Subsequent reactions of the addition adduct in the presence of O_2 then lead to the regeneration of HO radicals. In view of the possibility of a pressure dependence of the 298 K rate coefficient at low total pressures[3] (≤0.1 bar), the preferred values, which are identical to our previous evaluation, IUPAC, 1992,[4] are applicable to atmospheric conditions.

References

[1] G. Poulet, G. Laverdet, J. L. Jourdain, and G. Le Bras, J. Phys. Chem. **88**, 6259 (1984).
[2] M. J. Kurylo and G. L. Knable, J. Phys. Chem. **88**, 3305 (1984).
[3] A. J. Hynes and P. H. Wine, J. Phys. Chem. **95**, 1232 (1991).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO_2 + CH_3O_2 \rightarrow O_2 + CH_3O_2H$

[illegible] $= -156$ kJ·mol^{-1}

Rate coefficient data

[illegible] molecule^{-1} s^{-1}	Temp./K	Reference	Comments
[illegible] *Rate Coefficients*			
[illegible] 10^{-13} exp(862/T)	248–700	Lightfoot *et al.*, 1991[1]	(a)
[illegible] *and Evaluations*			
[illegible] 10^{-13} exp(780/T)	225–580	IUPAC, 1992[2]	(b)
[illegible] 10^{-13} exp(640/T)	228–573	Wallington, Dagaut, and Kurylo, 1992[3]	(c)
[illegible] 10^{-13} exp(790/T)	230–680	Lightfoot *et al.*, 1992[4]	(d)
[illegible] 10^{-13} exp(800/T)	200–300	NASA, 1994[5]	(e)

Comments

(a) Flash photolysis-UV absorption study of Cl_2-CH_3OH-CH_4-O_2-N_2 mixtures at 760 Torr and over the temperature range 600 to 719 K. The temperature dependent rate coefficient listed above was derived by the authors from a reanalysis of all of their data, including previous studies from flash photolysis experiments.

(b) k_{298} is the averaged value of Cox and Tyndall,[6] Jenkin *et al.*,[7] Dagaut *et al.*,[8] Moortgat *et al.*,[9] and Lightfoot *et al.*[10] and the temperature coefficient is that reported by Lightfoot *et al.*[10]

(c) Derived from an analysis of the data of Cox and Tyndall,[6] McAdam *et al.*,[11] Kurylo *et al.*,[12] Jenkin *et al.*,[7] Dagaut *et al.*,[8] Moortgat *et al.*,[9] and Lightfoot *et al.*[10]

(d) k_{298} is an average value of the data of Cox and Tyndall,[6] McAdam *et al.*,[11] Jenkin *et al.*,[7] Dagaut *et al.*,[8] Moortgat *et al.*,[9] and Lightfoot *et al.*[10]

(e) k_{298} is the averaged value of data from Cox and Tyndall,[6] McAdam *et al.*,[11] Kurylo *et al.*,[12] Jenkin *et al.*,[7] Moortgat *et al.*,[9] and Lightfoot *et al.*[10] E/R derived from the data of Cox and Tyndall,[6] Dagaut *et al.*,[8] and Lightfoot *et al.*[10]

Preferred Values

$k = 5.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.8 \times 10^{-13}$ exp(780/T) cm^3 molecule^{-1} s^{-1} over the temperature range 225–580 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

There have been no new data at or around room temperature and our previous recommendation,[2] which is in accord with other subsequent recommendations,[3–5] still stands. Wallington[13] has extended the previous FTIR study[14] of the products of the reaction at 760 Torr to a wider range of pressures (15–700 Torr) and confirmed that 92±5% of the $HO_2 + CH_3O_2$ reaction produces $O_2 + CH_3O_2H$. Wallington and Hurley[15] have shown from an FTIR study of the reaction between HO_2 and CD_3O_2 radicals that the sole product is CD_3OOH.

References

[1] P. D. Lightfoot, P. Roussel, F. Caralp, and R. Lesclaux, J. Chem. Soc. Faraday Trans. **87**, 3213 (1991).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).
[4] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).
[5] NASA Evaluation No. 11, 1994 (see references in Introduction).
[6] R. A. Cox and G. S. Tyndall, J. Chem. Soc. Faraday Trans. 2, **76**, 153 (1980).
[7] M. E. Jenkin, R. A. Cox, G. D. Hayman, and L. J. Whyte, J. Chem. Soc. Faraday Trans. 2, **84**, 913 (1988).
[8] P. Dagaut, T. J. Wallington, and M. J. Kurylo, J. Phys. Chem. **92**, 3833 (1988).
[9] G. K. Moortgat, R. A. Cox, G. Schuster, J. P. Burrows, and G. S. Tyndall, J. Chem. Soc. Faraday Trans. 2, **85**, 809 (1989).
[10] P. D. Lightfoot, B. Veyret, and R. Lesclaux, J. Phys. Chem. **94**, 708 (1990).
[11] K. McAdam, B. Veyret, and R. Lesclaux, Chem. Phys. Lett. **133**, 39 (1987).
[12] M. J. Kurylo, P. Dagaut, T. J. Wallington, and D. M. Neuman, Chem. Phys. Lett. **139**, 513 (1987).
[13] T. J. Wallington, J. Chem. Soc. Faraday Trans. **87**, 2379 (1991).
[14] T. J. Wallington and S. M. Japar, Chem. Phys. Lett. **167**, 513 (1990).
[15] T. J. Wallington and M. D. Hurley, Chem. Phys. Lett. **193**, 84 (1992).

$HO_2 + HOCH_2O_2 \rightarrow O_2 + HOCH_2O_2H$ (1)
$\rightarrow O_2 + HCO_2H + H_2O$ (2)

$\Delta H^\circ(2) = -473.1$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 1.2\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.6\times 10^{-15}$ exp(2300/T) cm^3 molecule^{-1} s^{-1} over the temperature range 275–335 K.
$k_2/k = 0.4$ at 298 K.

Reliability

$\Delta\log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 1500$ K.
$\Delta(k_1/k) = \pm 0.4$ at 298 K.

Comments on Preferred Values

The two studies[1,2] of the rate coefficient at 298 K are in good agreement and confirm that this reaction is fast compared with the HO_2 radical reactions with CH_3O_2 and $C_2H_5O_2$ radicals. The product channel yielding HCOOH is presumed to proceed via a six-membered cyclic intermediate, analogous to that proposed for the formation of HCHO, CH_3OH, and O_2 from the interaction of CH_3O_2 radicals. Both the temperature dependence and the branching ratio require independent confirmation. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K. Moortgat, J. Phys. Chem. **93**, 2368 (1989).
[2] J. P. Burrows, G. K. Moortgat, G. S. Tyndall, R. A. Cox, M. E. Jenkin, G.D. Hayman, and B. Veyret, J. Phys. Chem. **93**, 2375 (1989).
[3] M. E. Jenkin, R. A. Cox, G. D. Hayman, and L. J. Whyte, J. Chem. Soc. Faraday Trans. 2, **84**, 913 (1988).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO_2 + C_2H_5O_2 \rightarrow O_2 + C_2H_5O_2H$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.6×10^{-13} exp[(1260±130)/T]	248–480	Fenter *et al.*, 1993[1]	(a)
$(1.10\pm 0.21)\times 10^{-11}$	298		
6.9×10^{-13} exp[(702±69)/T]	210–363	Maricq and Szente, 1994[2]	(b)
$(8.3\pm 1.5)\times 10^{-12}$	295		
Reviews and Evaluations			
5.6×10^{-13} exp(650/T)	250–380	Wallington, Dagaut, and Kurylo, 1992[3]	(c)
6.5×10^{-13} exp(650/T)	250–380	Lightfoot *et al.*, 1992[4]	(d)
6.5×10^{-13} exp(650/T)	240–380	IUPAC, 1992[5]	(d)
7.5×10^{-13} exp(700/T)	200–300	NASA, 1994[6]	(e)

Comments

(a) Flash photolysis-UV absorption study of Cl_2-C_2H_6-O_2-N_2 mixtures at 760 Torr total pressure. Rate coefficients were derived from simultaneous computer analyses of several decay curves collected at different wavelengths.

(b) Flash photolysis-UV absorption study of F_2-H_2-C_2H_6-O_2-N_2 mixtures at a total pressure of ~200 Torr. Rate coefficients were derived from computer simulation of time-resolved decay curves.

(c) Based on the data of Dagaut *et al.*[7]

(d) The rate coefficient of $k = 5.8\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K was derived from the data of Cattell *et al.*[8] and Dagaut *et al.*,[7] together with $E/R = -650$ K from Dagaut *et al.*[7]

(e) Based on the rate coefficients of Cattell *et al.*,[8] Dagaut *et al.*,[7] Fenter *et al.*,[1] and Maricq and Szente.[2]

Preferred Values

$k = 7.7\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.7\times 10^{-13}$ exp(1000/T) cm^3 molecule^{-1} s^{-1} over the temperature range 200–500 K.

Reliability

$\Delta\log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The room temperature rate coefficients of Fenter *et al.*[1] and Maricq and Szente[2] are in reasonable agreement with the previous direct studies of Cattell *et al.*[8] and Dagaut *et al.*[7] We have based our recommendations on the average value of k_{298} from these four studies.[1,2,7,8] However, the temperature coefficients of Fenter *et al.*[1] and Maricq and Szente[2] differ by almost a factor of two, indicating a systematic error in one or both studies. We have recommended an E/R value corresponding to the rounded-off mean of these two studies,[1,2] but clearly more work is needed to resolve the difference.

As discussed in our previous evaluation,[5] the FTIR spectroscopic product study of Wallington and Japar[9] has shown this reaction has only one channel, to yield C_2H_5OOH + O_2.

References

[1] F. F. Fenter, V. Catoire, R. Lesclaux, and P. D. Lightfoot, J. Phys. Chem. **97**, 3530 (1993).
[2] M. M. Maricq and J. J. Szente, J. Phys. Chem. **98**, 2078 (1994).
[3] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).
[4] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).
[6] NASA Evaluation No. 11, 1994 (see references in Introduction).
[7] P. Dagaut, T. J. Wallington, and M. J. Kurylo, J. Phys. Chem. **92**, 3836 (1988).
[8] F. C. Cattell, J. Cavanagh, R. A. Cox, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. 2, **82**, 199 (1986).
[9] T. J. Wallington and S. M. Japar, Chem. Phys. Lett. **166**, 495 (1990).

$HO_2 + CH_3CO_3 \rightarrow O_2 + CH_3CO_3H$ (1)
$\rightarrow O_3 + CH_3CO_2H$ (2)

$\Delta H^\circ(2) = -132$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
4.3×10^{-13} exp[(1040±100)/T]	253–368	Moortgat, Veyret, and Lesclaux, 1989[1]	(a)
$(1.4\pm0.3)\times10^{-11}$	298		
Branching Ratios			
$k_2/k=0.23$	298	Niki *et al.*, 1985[2]	(b)
$k_2/k=0.33\pm0.07$	253–368	Moortgat, Veyret, and Lesclaux, 1989[1]	(c)
$k_2/k=8.5\times10^{-3}$ exp(1020/T)	263–333	Horie and Moortgat, 1992[2]	(d)
$k_2/k=0.26$	298		
Reviews and Evaluations			
4.3×10^{-13} exp(1040/T)	250–370	IUPAC, 1992[4]	(e)
$k_2/k=0.3$	250–370		(f)
4.3×10^{-13} exp(1040/T)	253–368	Wallington, Dagaut, and Kurylo, 1992[2]	(e)
$k_2/k=0.33$	253–300		(e)
4.3×10^{-13} exp(1040/T)	253–368	Lightfoot *et al.*, 1992[6]	(e)
$k_2/k=0.33$	253–368		(e)
4.5×10^{-13} exp(1000/T)	200–300	NASA, 1994[7]	(e)

Comments

(a) Flash photolysis of Cl_2 in the presence of CH_3CHO-CH_3OH-O_2-N_2 mixtures at total pressures of 600–650 Torr. [CH_3CO_3] was monitored by UV absorption over the wavelength range 195–280 nm and the absorption cross section measured relative to $\sigma(HO_2)=5.3\times10^{-18}$ cm^2 molecule^{-1} at 210 nm. Rate coefficients were derived from a computer simulation of absorption traces at a range of wavelengths, based on a mechanism including secondary removal of CH_3CO_3.

(b) FTIR study of irradiated Cl_2-HCHO-CH_3CHO-O_2 mixtures. The branching ratio was based on the analysis of the products CH_3CO_3H, CH_3CO_2H, and O_3.

(c) Derived from the same experiments as in Comment (a) by making allowance for absorption by O_3 product.

(d) FTIR study of irradiated $CH_3COCOCH_3$ in the presence of Ar-O_2 mixtures at total pressures of 730–770 Torr. The reaction products CO_2, CO, HCHO, HCOOH, CH_3CO_2H, CH_3CO_3H, CH_3OH, H_2O_2, and O_3 were analyzed by matrix-isolation FTIR spectroscopy combined with a molecular-beam sampling technique. The branching ratio obtained was $\ln(k_1/k_2)=\{(5.8\pm1.7)-[(1430\pm480)/T]\}$, derived from the yields of CH_3CO_3H and O_3.

(e) Based on the data of Moortgat *et al.*[1]

(f) Based on the data of Moortgat *et al.*[1] and Niki *et al.*[2]

Preferred Values

$k=1.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=4.3\times10^{-13}$ exp(1040/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.
$k_2/k=0.26$ at 298 K.
$k_2/k=8.5\times10^{-3}$ exp(1020/T) over the temperature range 260–340 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.
$\Delta(E_2/R - E/R) = \pm 500$ K.

Comments on Preferred Values

The recommended value of k together with its temperature dependence are unaltered since our last evaluation,[4] and are based on the data of Moortgat *et al.*[1] Independent confirmation is required to lower the error limits. The study of the products of the reaction by Horie and Moortgat,[3] leading to the measurement of the branching ratio, is much more direct than the previous study of Moortgat *et al.*[1] and, in contrast to the results of Moortgat *et al.*,[1] show a marked temperature dependence. The newer data[3] are in reasonable agreement with the room temperature measurements of the branching ratio made by Niki *et al.*[2]

References

[1] G. K. Moortgat, B. Veyret, and R. Lesclaux, Chem. Phys. Lett. **160**, 44 (1989).

[2] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys Chem. **89**, 588 (1985).

[3] O. Horie and G. K. Moortgat, J. Chem. Soc. Faraday Trans. **88**, 330 (1992).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

[5] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).

[6] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 180 (1992).

[7] NASA Evaluation No. 11, 1994 (see references in Introduction).

$HO_2 + HOCH_2CH_2O_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The studies of Murrells *et al.*[1] by laser flash photolysis and by molecular modulation of the absorption spectrum of the $HOCH_2CH_2O_2$ radical have shown that the absorption cross-sections reported earlier by Jenkin and Cox[2] from molecular modulation studies of the photolysis of $HOCH_2CH_2I$ are low by a factor of approximately 2. Jenkin and Cox[2] made the assumption that the photolysis of $HOCH_2CH_2I$ in their system yielded entirely $HOCH_2CH_2O_2$ radicals, which was apparently not the case. Increasing $\sigma_{230}(HOCH_2CH_2O_2)$ by a factor of two in the interpretation[1] of the data of Jenkin and Cox[2] yields the revised value of $k = (8.4 \pm 3.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

The recommended rate coefficient is the mean of this revised value together with the value of Murrells *et al.*[1] The approximate value derived by Anastasi *et al.*[3] in the pulsed radiolysis experiments is a factor of two higher than our recommended value, and we have not taken this value of Anastasi *et al.*[3] into account, owing to the differences in the absorption spectrum of the radical observed by Anastasi *et al.*[3] compared with the consistent spectra reported by Jenkin and Cox[2] and Murrells *et al.*[1] (see data for the reaction 2 $HOCH_2CH_2O_2 \rightarrow$ products). The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] T. P. Murrells, M. E. Jenkin, S. J. Shalliker, and G. D. Hayman, J. Chem. Soc. Faraday Trans. **87**, 2351 (1991).

[2] M. E. Jenkin and R. A. Cox, J. Phys. Chem. **95**, 3229 (1991).

[3] C. Anastasi, D. J. Muir, V. J. Simpson, and P. Pagsberg, J. Phys. Chem. **95**, 5791 (1991).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO_2 + CH_3OCH_2O_2 \rightarrow O_2 + CH_3OCH_2O_2H$ (1)
$\rightarrow O_2 + CH_3OCHO + H_2O$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Branching Ratios			
$k_1/k = 0.53 \pm 0.08$	295	Wallington *et al.*, 1993[1]	(a)
$k_2/k = 0.40 \pm 0.04$	295		

Comments

(a) HO_2 and $CH_3OCH_2O_2$ radicals were generated from the steady-state photolysis of Cl_2 in the presence of CH_3OH-CH_3OCH_3-O_2 mixtures at a total pressure of 900 Torr. Branching ratios were derived from FTIR analyses of CH_3OCHO and $CH_3OCH_2O_2H$ products, which accounted for 93±12% of the CH_3OCH_3 loss.

Preferred Values

$k_1/k = 0.60$ at 298 K.
$k_2/k = 0.40$ at 298 K.

Reliability
$\Delta(k_1/k) = \pm 0.10$ at 298 K.
$\Delta(k_2/k) = \pm 0.10$ at 298 K.

Comments on Preferred Values

The reaction between HO_2 radicals and $CH_3OCH_2O_2$ radicals is analogous to that between HO_2 radicals and $HOCH_2O_2$ radicals in that there are two channels of nearly equal importance at room temperature, producing (i) the hydroperoxide plus O_2 and (ii) a carbonyl product, H_2O and O_2. In contrast, the HO_2 reactions with unsubstituted alkyl peroxy radicals, RO_2, appear to have only a single channel, producing the alkyl hydroperoxide.

It has been proposed[1] that the reaction between HO_2 and substituted RO_2 radicals yielding the carbonyl compounds proceeds through a six-member transition state identical to that suggested by Russell[2] to explain the molecular products from the interactions of RO_2 radicals.

References

[1] T. J. Wallington, M. D. Hurley, J. C. Ball, and M. E. Jenkin, Chem. Phys. Lett. **211**, 41 (1993).
[2] G. Russell, J. Am. Chem. Soc. **79**, 3871 (1957).

$HO_2 + CH_3COCH_2O_2 \rightarrow O_2 + CH_3COCH_2O_2H$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.0\pm1.3)\times10^{-12}$	298	Bridier *et al.*, 1993[1]	(a)

Comments

(a) Flash photolysis of Cl_2 in the presence of CH_3COCH_3-CH_3OH-N_2 mixtures at a total pressure of 760 Torr. The rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 210 and 230 nm.

Preferred Values

$k = 9.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

While the above value of the rate coefficient seems reasonable, it has been obtained from the kinetic analysis of a complex chemical system and requires independent verification to reduce the recommended error limits. No evidence was obtained by Bridier *et al.*[1] for products other than O_2 and $CH_3COCH_2O_2H$.

References

[1] I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. **89**, 2993 (1993).

$HO_2 + HCHO \rightarrow HOCH_2OO$

$\Delta H^\circ = -68.1$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=7.9\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=9.7\times10^{-15}$ exp$(625/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 275–333 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(E/R)=\pm600$ K.

Comments on Preferred Values

This data sheet is based on our previous evaluation, IUPAC, 1989.[1] The most recent studies of Barnes *et al.*[2] and Veyret *et al.*[3] are in excellent agreement regarding this rate coefficient, and both are in good agreement with the earlier data of Veyret *et al.*[4] The preferred rate equation is derived by taking an average value of the rate coefficients of Barnes *et al.*[2] [k(273 K)$=1.1\times10^{-13}$ cm^3 molecule^{-1} s^{-1}] and of Veyret *et al.*[3] [k(275 K)$=8.0\times10^{-14}$ cm molecule^{-1} s^{1}] together with the value of *E/R* determined b Veyret *et al.*[3] The preferred values are identical to our previous evaluation, IUPAC, 1992.[5]

This reaction is believed to proceed via the initial formation of the adduct radical, HO_2CH_2O, *which rapidly isomerizes* to the product radical, $HOCH_2OO$ via H-atom transfer

References

[1] IUPAC, Supplement III, 1989 (see references in Introduction).
[2] I. Barnes, K. H. Becker, E. H. Fink, A. Reimer, F. Zabel, and H. Nik Chem. Phys. Lett. **115**, 1 (1985).
[3] B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K Moortgat, J. Phys. Chem. **93**, 2368 (1989).
[4] B. Veyret, J.-C. Rayez, and R. Lesclaux, J. Phys. Chem. **86**, 3424 (198
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HOCH_2OO \rightarrow HO_2 + HCHO$

$\Delta H^\circ=68.1$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=1.5\times10^{2}$ s^{-1} at 298 K.
$k=2.4\times10^{12}$ exp$(-7000/T)$ s^{-1} over the temperature range 275–333 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(E/R)=\pm2000$ K.

Comments on Preferred Values

This data sheet is based on our previous evaluation, IUPAC, 1989.[1] The studies of Barnes *et al.*[2] and Veyret *et al.*[3] are in good agreement regarding the rate coefficient of this reaction. The preferred rate equation has been obtained by taking the average of the rate coefficients at 273 K from these studies together with the *E/R* determined by Veyret *et al.*[3] The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

It should be pointed out that the equilibrium constant, K_1, for the reactions $HO_2+HCHO\rightleftarrows HOCH_2O_2$ (1,−1), $K_1=5.2\times10^{-16}$ cm^3 molecule^{-1} at 298 K, derived from the kinetic study of Veyret *et al.*[3] (which is identical to the value obtained from our recommended data for k_1 and k_{-1}), is in excellent agreement with the value of $K_1=4.0\times10^{-16}$ cm^3 molecule^{-1} at 298 K obtained independently by Burrows *et al.*[5] from molecular modulation studies. The above value of K_1 is, however, considerably smaller than the value of $K_1=3.4\times10^{-15}$ cm^3 molecule^{-1} at 298 K reported by Zabel *et al.*[6] from EPR spectroscopic measurements of the ratio of concentrations of HO_2 and $HOCH_2OO$ radicals in the photolysis of $HCHO$-O_2 mixtures.

References

[1] IUPAC, Supplement III, 1989 (see references in Introduction).
[2] I. Barnes, K. H. Becker, E. H. Fink, A. Reimer, F. Zabel, and H. Niki, Chem. Phys. Lett. **115**, 1 (1985).
[3] B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K. Moortgat, J. Phys. Chem. **93**, 2368 (1989).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).
[5] J. P. Burrows, G. K. Moortgat, G. S. Tyndall, R. A. Cox, M. E. Jenkin, G.D. Hayman, and B. Veyret, J. Phys. Chem. **93**, 2375 (1989).
[6] F. Zabel, K. A. Sahetchian, and C. Chachaty, Chem. Phys. Lett. **134**, 433 (1987).

$NO_3 + CH_4 \rightarrow HNO_3 + CH_3$

$\Delta H^\circ = 12.0\ kJ \cdot mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 4 \times 10^{-16}$	298	Burrows, Tyndall, and Moortgat, 1985[1]	(a)
$\leq 2 \times 10^{-17}$	298±2	Wallington *et al.*, 1986[2]	(b)
$\leq 8 \times 10^{-19}$	302	Boyd *et al.*, 1991[3]	(c)
Relative Rate Coefficients			
$\leq 6 \times 10^{-21}$	~298	Cantrell *et al.*, 1987[4]	(d)
Reviews and Evaluations			
$\leq 1 \times 10^{-18}$	298	Atkinson, 1991[5]	(e)

Comments

(a) NO_3 radicals were generated by the modulated photolysis of Cl_2-$ClONO_2$-N_2 or F_2-HNO_3-N_2 mixtures and monitored by optical absorption at 662 nm.

(b) NO_3 radicals were generated by the flash photolysis of $ClONO_2$-He mixtures and detected by optical absorption at 662 nm.

(c) Stopped-flow system with optical absorption detection of NO_3 radicals at 662 nm. Occurrence of secondary reactions were expected to lead to a stoichiometry factor of ≥ 2, resulting in the upper limit to the rate coefficient cited in the table.

(d) Relative rate method. Upper limit to the rate coefficient was derived from the absence of CO and CO_2 formation after addition of CH_4 to N_2O_5-NO_3-NO_2-N_2 mixtures. An equilibrium constant for the $NO_2 + NO_3 \rightleftarrows N_2O_5$ reactions of $3.41 \times 10^{-11}\ cm^3\ molecule^{-1}$ at 298 K[5] has been used to derive the rate coefficient cited.

(e) Based on the upper limits derived by Burrows *et al.*,[1] Wallington *et al.*,[2] and Cantrell *et al.*[4]

Preferred Values

$k < 1 \times 10^{-18}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

Comments on Preferred Values

The preferred value is based on the upper limits to the rate coefficients obtained by Cantrell *et al.*[4] and Boyd *et al.*,[3] and is consistent with the higher upper limits reported by Burrows *et al.*[1] and Wallington *et al.*[2]

References

[1] J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, J. Phys. Chem. **89**, 4848 (1985).

[2] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 4640 (1986).

[3] A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, J. Chem. Soc. Faraday Trans. **87**, 2913 (1991).

[4] C. A. Cantrell, J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert, J. Phys. Chem. **91**, 6017 (1987).

[5] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

$NO_3 + C_2H_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k < 1 \times 10^{-16}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

Comments on Preferred Values

The measurement of rate coefficients for low reactivity organics is complicated by the possibility of secondary reactions, leading to erroneously high measured rate coefficients. The relative rate measurements of Atkinson *et al.*[1] show C_2H_2 to be significantly less reactive than C_2H_4. The preferred value of the upper limit to the rate coefficient is sufficiently high to be consistent with the data of Canosa-Mas *et al.*[2] Until there are confirmatory data for the reported temperature dependence[3] of this rate coefficient, no temperature dependence is recommended. The preferred value is identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] R. Atkinson, S. M. Aschmann, and M. A. Goodman, Int. J. Chem. Kinet. **19**, 299 (1987).

[2] C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **84**, 247 (1988).

[3] C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc Faraday Trans. 2, **84**, 263 (1988).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO_3 + C_2H_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.7\pm0.5)\times10^{-16}$	300	Biggs *et al.*, 1991;[1] Boyd *et al.*, 1991[2]	(a)
Reviews and Evaluations			
$3.3\times10^{-12}\exp(-2880/T)$	270–340	IUPAC, 1992[3]	(b)
$4.88\times10^{-18}\,T^2\exp(-2282/T)$	295–523	Atkinson, 1994[4]	(c)

Comments

(a) Stopped-flow technique with optical absorption of the NO_3 radical at 662 nm. The influence of the reaction $NO_2 + NO_3 + He \rightarrow N_2O_5 + He$ was taken into account by numerical modeling, leading to a stoichiometry factor for NO_3 radical decays of ~1.9 and the cited rate coefficient for the elementary NO_3 + ethene reaction.

(b) Based on the absolute rate coefficients of Canosa-Mas *et al.*[5,6] and the relative rate coefficient of Atkinson *et al.*[7] These data[5–7] were fitted to the three-parameter expression $k=CT^2\exp(-D/T)$, resulting in $k=4.88\times10^{-18}\,T^2\exp(-2282/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 295–523 K. The Arrhenius expression, $k=A\times\exp(-B/T)$, was centered at 300 K and was derived from the three-parameter expression with $A=C\,e^2\,T^2$ and $B=D+2T$.

(c) Derived from the absolute rate coefficients of Canosa-Mas *et al.*[5,6] and the relative rate coefficient of Atkinson *et al.*,[7] using the three parameter expression $k=CT^2\exp(-D/T)$.

Preferred Values

$k=2.1\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=3.3\times10^{-12}\exp(-2880/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The preferred rate coefficient is derived using the absolute rate coefficient data of Canosa-Mas *et al.*[5,6] and the relative rate coefficient of Atkinson *et al.*[7] These data were fitted to the three parameter expression $k=CT^2\exp(-D/T)$, resulting in $k=4.88\times10^{-18}\,T^2\exp(-2282/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 295–523 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$, is centered at 300 K and is derived from the three parameter expression with $A=C\,e^2\,T^2$ and $B=D+2T$.

The preferred rate coefficient is in agreement with the 300 K rate coefficient of Biggs *et al.*[1] and Boyd *et al.*,[2] and the preferred values are identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] P. Biggs, A. A. Boyd, C. E. Canosa-Mas, D. M. Joseph, and R. P. Wayne, Meas. Sci. Technol. **2**, 675 (1991).

[2] A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, J. Chem. Soc. Faraday Trans. **87**, 2913 (1991).

[3] IUPAC, Supplement IV, 1992 (see reference in Introduction).

[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[5] C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **84**, 247 (1988).

[6] C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **84**, 263 (1988).

[7] R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., J. Phys. Chem. **92**, 3454 (1988).

$NO_3 + C_2H_6 \rightarrow HNO_3 + C_2H_5$

$\Delta H^\circ = 3.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 4\times 10^{-18}$	298±2	Wallington *et al.*, 1986[1]	(a)
$5.7\times 10^{-12}\exp[-(4426\pm 337)/T]$	453–553	Bagley *et al.*, 1990[2]	(b)
$\leq (2.7\pm 0.2)\times 10^{-17}$	302	Boyd *et al.*, 1991[3]	(c)

Comments

(a) NO_3 radicals were generated by the flash photolysis of $ClONO_2$-He mixtures and detected by optical absorption at 662 nm.

(b) Discharge flow system with detection of NO_3 radicals by optical absorption at 662 nm.

(c) Stopped-flow system with optical absorption detection of the NO_3 radical at 662 nm. Secondary reactions were expected to lead to a stoichiometry factor of ≈ 2, leading to the cited upper limit to the rate coefficient.

Preferred Values

$k < 1\times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

Extrapolation of the absolute rate coefficients obtained by Bagley *et al.*[2] over the temperature range 453–553 K to 298 K leads to a 298 K rate coefficient of 2×10^{-18} cm^3 molecule^{-1} s^{-1}, probably uncertain to at least a factor of 2 due to the long extrapolation and possible non-Arrhenius behavior of the rate coefficient for this reaction. The preferred upper limit is based on the upper limit of Wallington *et al.*[1] and extrapolation to 298 K of the elevated temperature rate coefficients of Bagley *et al.*[2]

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 4640 (1986).

[2] J. A. Bagley, C. Canosa-Mas, M. R. Little, A. D. Parr, S. J. Smith, S. J. Waygood, and R. P. Wayne, J. Chem. Soc. Faraday Trans. **86**, 2109 (1990).

[3] A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, J. Chem. Soc. Faraday Trans. **87**, 2913 (1991).

$NO_3 + C_3H_6 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.74\times 10^{-13}\exp[-(1171\pm 66)/T]$	298–423	Canosa-Mas *et al.*, 1991[1]	(a)
$(9.3\pm 1.2)\times 10^{-15}$	298		
Reviews and Evaluations			
9.4×10^{-15}	298	IUPAC, 1992[2]	(b)
$4.59\times 10^{-13}\exp(-1156/T)$	296–423	Atkinson, 1994[3]	(c)

Comments

(a) Discharge flow system with optical absorption detection of the NO_3 radical at 662 nm. Rate coefficients were measured over the temperature range 298–523 K, and the Arrhenius plot exhibited curvature above 423 K.

(b) Based on the relative rate coefficient study of Atkinson *et al.*[4]

(c) Derived using the room temperature relative rate coefficient of Atkinson *et al.*[4] and the absolute rate coefficients of Canosa-Mas *et al.*[1] over the temperature range 298–423 K. These rate coefficients[1,4] were fitted to an Arrhenius expression.

Preferred Values

$k=9.5\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=4.6\times10^{-13}\exp(-1155/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 296–423 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The preferred values are derived using the room temperature relative rate coefficient of Atkinson *et al.*[4] and the 298–423 K absolute rate coefficients of Canosa-Mas *et al.*[1] The preferred 298 K rate coefficient is in agreement with the previous relative rate measurements of Morris and Niki,[5] Japar and Niki,[6] and Atkinson *et al.*[7] when the differing values of the equilibrium constant used for the $N_2O_5 \rightleftarrows NO_3 + NO_2$ reactions are taken into account.

The NO_3 radical reaction with propene proceeds by initial addition, leading to the formation under simulated trop spheric conditions of HCHO, CH_3CHO, an $CH_3COCH_2ONO_2$.[3,8–11]

References

[1] C. E. Canosa-Mas, S. J. Smith, S. J. Waygood, and R. P. Wayne, J. Che Soc. Faraday Trans. **87**, 3473 (1991).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[4] R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., J. Phys. Chem. **92**, 34 (1988).

[5] E. D. Morris, Jr. and H. Niki, J. Phys. Chem. **78**, 1337 (1974).

[6] S. M. Japar and H. Niki, J. Phys. Chem. **79**, 1629 (1975).

[7] R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, J J. Phys. Chem. **88**, 1210 (1984).

[8] H. Bandow, M. Okuda, and H. Akimoto, J. Phys. Chem. **84**, 3604 (198

[9] P. B. Shepson, E. O. Edney, T. E. Kleindienst, J. H. Pittman, G. R. Nam and L. T. Cupitt, Environ. Sci. Technol. **19**, 849 (1985).

[10] I. Barnes, V. Bastian, K. H. Becker, and Z. Tong, J. Phys. Chem. **94**, 241 (1990).

[11] J. Hjorth, C. Lohse, C. J. Nielsen, H. Skov, and G. Restelli, J. Phys. Chem **94**, 7494 (1990).

$NO_3 + C_3H_8 \rightarrow HNO_3 + n\text{-}C_3H_7$ (1)

$\rightarrow HNO_3 + \text{iso-}C_3H_7$ (2)

$\Delta H^\circ(1)=-6.8$ kJ·mol^{-1}

$\Delta H^\circ(2)=-14.3$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq(4.8\pm1.7)\times10^{-17}$	298	Boyd *et al.*, 1991[1]	(a)

Comments

(a) Stopped-flow system with optical absorption detection of the NO_3 radical at 662 nm. The occurrence of secondary reactions is expected to lead to a stoichiometry factor of $\geqslant2$, resulting in the upper limit to the rate coefficient cited in the table.

Preferred Values

$k<7\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

Based on the upper limit derived by Boyd *et al.*[1]

References

[1] A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, J. Chem. Soc. Faraday Trans. **87**, 2913 (1991).

$NO_3 + HCHO \rightarrow HNO_3 + HCO$

$\Delta H^\circ=-58.4$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 5.8 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The data of Atkinson *et al.*,[1] Cantrell *et al.*,[2] and Hjorth *et al.*[3] disagree by a factor of ~1.5 when the same equilibrium constant for the reactions $NO_2 + NO_3 \rightleftarrows N_2O_5$ is used to place the rate coefficients on an absolute basis. However, the rate coefficient obtained by Cantrell *et al.*[2] from experiments which were independent of this equilibrium constant agree well with that derived from the Atkinson *et al.*[1] data. Accordingly, a rate coefficient of 5.8×10^{-16} cm^3 molecule^{-1} s^{-1} is recommended, with the uncertainty limits reflecting the need for an absolute measurement. The preferred value is identical to our previous evaluation, IUPAC, 1992.[4] While no temperature dependence of the rate coefficient has been measured to date, by analogy with the NO_3 radical reaction with CH_3CHO, a preexponential factor of $\sim 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is expected, and hence $k(NO_3 + HCHO) \sim 2 \times 10^{-12} \exp(-2430/T)$ cm^3 molecule^{-1} s^{-1}.

This reaction proceeds by H-atom abstraction.

$$NO_3 + HCHO \rightarrow HNO_3 + HCO$$

References

[1] R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **88**, 1210 (1984).
[2] C. A. Cantrell, W. R. Stockwell, L. G. Anderson, K. L. Busarow, D. Perner, A. Schmeltekopf, J. G. Calvert, and H. S. Johnston, J. Phys. Chem. **89**, 139 (1985).
[3] J. Hjorth, G. Ottobrini, and G. Restelli, J. Phys. Chem. **92**, 2669 (1988).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO_3 + CH_3CHO \rightarrow HNO_3 + CH_3CO$

$\Delta H° = -67.3$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 2.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.4 \times 10^{-12} \exp(-1860/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–370 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are based upon the sole absolute rate coefficient study of Dlugokencky and Howard.[1] The rate coefficients reported by Morris and Niki,[2] Atkinson *et al.*,[3] and Cantrell *et al.*[4] (when reevaluated[5] to be consistent with recent values of the equilibrium constant for the $NO_2 + NO_3 \rightleftarrows N_2O_5$ reactions) are in good agreement with this preferred value. However, because of the significant uncertainties in this equilibrium constant,[5] these relative rate coefficient data were not used in the evaluation of the preferred rate coefficient. The preferred values are identical to our previous evaluation, IUPAC, 1992.[6]

References

[1] E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **93**, 1091 (1989).
[2] E. D. Morris, Jr. and H. Niki, J. Phys. Chem. **78**, 1337 (1974).
[3] R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **88**, 1210 (1984).
[4] C. A. Cantrell, J. A. Davidson, K. L. Busarow, and J. G. Calvert, J. Geophys. Res. **91**, 5347 (1986).
[5] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO_3 + CH_3COCH_3 \rightarrow HNO_3 + CH_3COCH_2$

$\Delta H° = -15.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq (8.5 \pm 2.5) \times 10^{-18}$	302	Boyd *et al.*, 1991[1]	(a)

Comments

(a) Stopped flow system with detection of the NO_3 radical by optical absorption at 662 nm. Secondary reactions were believed to be important and a stoichiometry factor of ≥ 2 has been used to obtain the cited upper limit to the rate coefficient.

Preferred Values

$k < 3 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The upper limit to the preferred value is derived from the measured overall rate coefficient of $(1.7 \pm 0.5) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}, with no account taken of the expected greater than unity stoichiometry.

References

[1] A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, J. Chem. Soc. Faraday Trans. **87**, 2913 (1991).

$NO_3 + CH_3OH \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k = 2.4 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3 \times 10^{-12} \exp(-2560/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–480 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 700$ K.

Comments on Preferred Values

The preferred values are based on the absolute rate coefficient study of Canosa-Mas *et al.*,[1] and are identical to our previous evaluation, IUPAC, 1992.[2] The 298 K preferred rate coefficient is consistent with the upper limit to the rate coefficient determined by Wallington *et al.*[3]

References

[1] C. E. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **85**, 709 (1989).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **19**, 243 (1987).

$NO_3 + C_2H_5OH \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k < 2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the only study carried out to date,[1] and is identical to our previous evaluation, IUPAC, 1992.[2] A somewhat higher upper limit is recommended than cited by Wallington *et al.*[1]

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **19**, 243 (1987).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO_3 + i\text{-}C_3H_7OH \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k < 5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the only study carried out to date,[1] and is identical to our previous evaluation, IUPAC, 1992.[2] A somewhat higher upper limit is recommended than cited by Wallington *et al.*[1]

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **19**, 243 (1987).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$

$\Delta H^\circ = -135.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
[illegible] $\times 10^{-31}$ $(T/300)^{-3.64\pm1.0}$ [N_2]	264–370	Kaiser, 1993[1]	(a)
Reviews and Evaluations			
$1.0\times10^{-30}(T/300)^{-3.3}$ [N_2]	200–300	IUPAC, 1992[2]	(b)
$4.5\times10^{-31}(T/300)^{-3.0}$ [Air]	200–300	NASA, 1994[3]	(c)

Comments

(a) Irradiation of CH_4-Cl_2-O_2-N_2 mixtures with a fluorescence lamp. CH_4 and CH_3Cl were analyzed by GC. Rate constants were measured relative to the reaction $CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$ [$k=3.95\times10^{-12} \times \exp(-267/T)$ cm^3 molecule^{-1} s^{-1}].[4,5] Falloff extrapolations were carried out with F_c values of 0.48, 0.46, and 0.42 at 264, 297, and 370 K, respectively.

(b) Based on the results of Ref. 6 which were in good agreement with the previous preferred values of Ref. 7.

(c) This value was based on a previous compilation,[8] and mainly on the data from Keiffer *et al.*[6]

Preferred Values

$k_0=1.0\times10^{-30}(T/300)^{-3.3}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_0=\pm0.2$ at 298 K.

$\Delta n=\pm1$.

Comments on Preferred Values

The recent values of Kaiser[1] agree very well with our previous evaluation, IUPAC, 1992,[2] which remains unchanged.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.31\pm0.1)\times10^{-12}$ $(T/300)^{1.2\pm0.8}$	264–370	Kaiser, 1993[1]	(a)
Reviews and Evaluations			
2.2×10^{-12} $(T/300)^{1.0}$	200–400	IUPAC, 1992[2]	(b)
1.8×10^{-12} $(T/300)^{-1.7}$	200–300	NASA, 1994[3]	(c)

Comments

(a) See comment (a) for k_0.

(b) Values based on Refs. 7 and 9 which have been extrapolated to high pressures with $F_c=0.27$ at 300 K.

(c) This value fits the data from Refs. 6 and 9. The temperature dependence was estimated. Extrapolation with $F_c=0.6$.

Preferred Values

$k_\infty=1.8\times10^{-12}$ $(T/300)^{1.1}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_\infty=\pm0.3$.

$\Delta n=\pm1$.

Comments on Preferred Values

The preferred value is an average of earlier results from Refs. 6 and 9 and the more recent determination by Kaiser.[1]

References

[1] E. W. Kaiser, J. Phys. Chem. **97**, 11681 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] L. J. Kovalenko and S. R. Leone, J. Chem. Phys. **80**, 3656 (1984).

[5] R. S. Timonen and D. Gutman, J. Phys. Chem. **90**, 2987 (1986).

[6] M. Keiffer, M. J. Pilling, and M. J. C. Smith, J. Phys. Chem. **91**, 6028 (1987).

[7] IUPAC, Supplement III, 1989 (see references in Introduction).

[8] NASA Evaluation No. 9, 1990 (see references in Introduction).

[9] C. J. Cobos, H. Hippler, K. Luther, A. R. Ravishankara, and J. Troe, J. Phys. Chem. **89**, 4332 (1985).

$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$

$\Delta H° = -54.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 3.8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.
$k = 1.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K and 0.133 bar.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The recommended pressure-dependent values of k_{298} are from the product study of Kaiser *et al.*,[1] and are identical to our previous evaluation, IUPAC, 1992.[2] The temperature dependence of the rate coefficient has yet to be established, but at a given pressure, increasing the temperature leads to an increased yield of C_2H_4.

For a full discussion on the mechanism of the $C_2H_5 + O$ reaction see the paper of Wagner *et al.*[3] It is clear that for atmospheric conditions the interaction of C_2H_5 with O_2 to form $C_2H_5O_2$ radicals is by far the dominant pathway.

References

[1] E. W. Kaiser, I. M. Lorkovic, and T. J. Wallington, J. Phys. Chem. 94 3352 (1990).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] A. F. Wagner, I. R. Slagle, D. Sarzynski, and D. Gutman, J. Phys. Chem **94**, 1853 (1990).

$C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$

$\Delta H° = -150.2$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 5.9 \times 10^{-29}\ (T/300)^{-3.8}\ [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

Experiments so far have mainly been conducted in the bath gas He, the previously recommended rate coefficients[1] for M = N_2 and O_2 being estimated relative to the He data. The new study of Ref. 2 reports identical rate coefficients for M = He and N_2 in the upper-half of the falloff curve. For this reason we revised the preferred values by using identical k_0 values for M = He and N_2. We prefer the most extensive results from Ref. 3 because the long falloff extrapolation to k_0 was done with a careful theoretical analysis. However, we retain the temperature coefficient from Ref. 4 which was determined theoretically. Falloff extrapolations were made with theoretically derived[3] values of $F_c = 0.64$ at 200 K and 0.54 at 300 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 7.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over the temperature range 200–300 K.

Comments on Preferred Values

As for k_0, we prefer the most extensive data from Ref. 3 because of their combination with a careful theoretical analysis. We assume a temperature independent rate coefficient k_∞ below 300 K. Falloff curves were fitted[3] with an expression $F_c = \{0.58 \exp(-T/1250) + 0.42 \exp(-T/183)\}$ which leads to $F_c = 0.64$ at 200 K and 0.54 at 300 K. Within the stated error limits, the available data all agree with the preferred values based on Ref. 3. QRRK calculations[4] of the reaction are less realistic than the RRKM calculations of Ref. 3. The analysis of the reaction system is complicated because there is a coupling of the addition reaction with the reaction forming C_2H_4, i.e., $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$, see the analysis in Ref. 3. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.[5]

References

[1] IUPAC, Supplement III, 1989 (see references in Introduction).
[2] E. W. Kaiser, T. J. Wallington, and J. M. Andino, Chem. Phys. Lett. **168**, 309 (1990).
[3] A. F. Wagner, I. R. Slagle, D. Sarzynski, and D. Gutman, J. Phys. Chem. **94**, 1853 (1990).
[4] J. W. Bozzelli and A. M. Dean, J. Phys. Chem. **94**, 3313 (1990).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$n\text{-}C_3H_7 + O_2 + M \rightarrow n\text{-}C_3H_7O_2 + M$

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k = 6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 1–10 Torr and 298 K.
$k_\infty = 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over the range 200–300 K.

Comments on Preferred Values

The available experimental data are consistent with each other.[1,2] Because they were obtained at total pressures below 100 Torr, we estimate that some falloff corrections have to be applied and these are taken into account in the preferred values. These values are consistent with experiments for the reactions $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ and $i\text{-}C_3H_7 + O_2 + M \rightarrow i\text{-}C_3H_7O_2 + M$ (see this evaluation). These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] R. P. Ruiz and K. D. Bayes, J. Phys. Chem. **88**, 2592 (1984).
[2] I. R. Slagle, J.-Y. Park, and D. Gutman, *20th International Symposium on Combustion, 1984* (Combustion Institute, Pittsburgh, PA, 1985), pp. 733–741.
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$i\text{-}C_3H_7 + O_2 + M \rightarrow i\text{-}C_3H_7O_2 + M$

$\Delta H^\circ = -158.9$ kJ·mol^{-1}

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

The preferred values are the average of the results from Refs. 1 and 2. Falloff corrections are probably within the uncertainties of the average. The rate coefficient k_∞ for this reaction appears consistent with those for the reactions $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ and $n\text{-}C_3H_7 + O_2 + M \rightarrow n\text{-}C_3H_7O_2 + M$ (see this evaluation). These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] R. P. Ruiz and K. D. Bayes, J. Phys. Chem. **88**, 2592 (1984).
[2] J. Munk, P. Pagsberg, E. Ratajczak, and A. Sillesen, Chem. Phys. Lett. **132**, 417 (1986).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_3COCH_2 + O_2 + M \rightarrow CH_3COCH_2O_2 + M$

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 1.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 300 K.

Comments on Preferred Values

The preferred values are based on the study of Cox *et al.*[1] Because this is the only study of this reaction, we indicate large error limits. Near atmospheric pressure this reaction should be close to the high pressure limit. These preferred values are identical to those in our previous evaluation IUPAC, 1992.[2]

References

[1] R. A. Cox, J. Munk, O. J. Nielsen, P. Pagsberg, and E. Ratajczak, Chem. Phys. Lett. **173**, 206 (1990).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HCO + O_2 \rightarrow CO + HO_2$

$\Delta H^\circ = -137.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The most recent measurements of the room temperature rate coefficient[1,2] are in good agreement with our previous recommendation.[3] The preferred temperature-independent rate coefficient is the average of the room-temperature rate coefficients of Washida *et al.*,[4] Shibuya *et al.*,[5] Veyret and Lesclaux,[6] Timonen *et al.*,[1] and Stief *et al.*,[2] and is identical to our previous evaluation, IUPAC, 1992.[7] Taken together, the temperature-dependent studies of Veyret and Lesclaux,[6] Timonen *et al.*,[1] and Stief *et al.*[2] show that the rate coefficient of this reaction is essentially independent of temperature over the temperature range 200–400 K, within the error limits of the measurements.

References

[1] R. S. Timonen, E. Ratajczak, and D. Gutman, J. Phys. Chem. **92**, 651 (1988).

[2] L. J. Stief, F. L. Nesbitt, and J. F. Gleason, abstracts of papers presented at the International Symposium of Gas Kinetics, Assisi, Italy, September 1990.

[3] CODATA, Supplement II, 1984; IUPAC, Supplement III, 1989 (see references in Introduction).

[4] N. Washida, R. I. Martinez, and K. D. Bayes, Z. Naturforsch. Teil A *29*, 251 (1974).

[5] K. Shibuya, T. Ebata, K. Obi, and I. Tanaka, J. Phys. Chem. **81**, 2292 (1977).

[6] B. Veyret and R. Lesclaux, J. Phys. Chem. **85**, 1918 (1981).

[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_3CO + O_2 + M \rightarrow CH_3CO_3 + M$

$\Delta H^\circ = -148$ kJ·mol^{-1}

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k = 2.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1–4 Torr.

$k_\infty = 5.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ over the temperature range 200–300 K.

Comments on Preferred Values

The preferred values are based on Ref. 1 with some falloff correction estimated by comparison with the reaction $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ (see this evaluation). These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[2]

References

[1] C. E. McDade, T. M. Lenhardt, and K. D. Bayes, J. Photochem. **20**, 1 (1982).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_2OH + O_2 \rightarrow HCHO + HO_2$

$\Delta H^\circ = -85.0$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 9.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.

Comments on Preferred Values

The rate coefficient at 298 K is now well established for this reaction, and our recommendation is the average of the results of Grotheer *et al.*,[1] Nesbitt *et al.*,[2] Pagsberg *et al.*,[3] Miyoshi *et al.*,[4] Grotheer *et al.*,[5] Dóbé *et al.*,[6] and Payne *et al.*,[7] and is identical to our previous evaluation, IUPAC, 1992.[8] The earlier data of Wang *et al.*[9] and Radford *et al.*[10] are rejected on the basis that they involved high concentrations of radicals, leading to mechanistic complications.[11] The two recent studies[1,2] of the temperature dependence of this reaction indicate that the rate coefficient follows a complicated non-Arrhenius behavior over the range 200–700 K. The existing data are difficult to explain and more work is needed to confirm the observed temperature dependence of this reaction before a recommendation can be made.

Grotheer *et al.*[1] have carried out experiments replacing CH_3OH by CH_3OD and have observed no kinetic effect for the $CH_2OH/CH_2OD + O_2$ reactions.

References

[1] H.-H. Grotheer, G. Riekert, D. Walter, and Th. Just, J. Phys. Chem. **92**, 4028 (1988); *22nd International Symposium on Combustion, 1988* (Combustion Institute, Pittsburgh, PA, 1989), pp. 963–972.

[2] F. L. Nesbitt, W. A. Payne, and L. J. Stief, J. Phys. Chem. **92**, 4030 (1988).

[3] P. Pagsberg, J. Munk, C. Anastasi, and V. J. Simpson, J. Phys. Chem. **93**, 5162 (1989).

[4] A. Miyoshi, H. Matsui, and N. Washida, J. Phys. Chem. **94**, 3016 (1990).

[5] H.-H. Grotheer, G. Riekert, U. Meier, and Th. Just, Ber. Bunsenges. Phys. Chem. **89**, 187 (1985).

[6] S. Dóbé, F. Temps, T. Böhland, and H. Gg. Wagner, Z. Naturforsch. Teil A **40**, 1289 (1985).

[7] W. A. Payne, J. Brunning, M. B. Mitchell, and L. J. Stief, Int. J. Chem. Kinet. **20**, 63 (1988).

[8] IUPAC, Supplement IV, 1992 (see references in Introduction).

[9] W. C. Wang, M. Suto, and L. C. Lee, J. Chem. Phys. **81**, 3122 (1984).

[10] H. E. Radford, Chem. Phys. Lett. **71**, 195 (1980).

[11] IUPAC, Supplement III, 1989 (see references in Introduction).

$CH_3CHOH + O_2 \rightarrow CH_3CHO + HO_2$

$\Delta H^\circ = -87.6$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value of k_{298} is the mean of the results of Grotheer *et al.*,[1] Anastasi *et al.*,[2] and Miyoshi *et al.*,[3] and is identical to our previous evaluation, IUPAC, 1992.[4] The rather large discrepancy between the data of Miyoshi *et al.*[3] and the other two studies[1,2] could be due to the different sources of generation of the CH_3CHOH radical. CH_3CHOH radical generation[1,2] involving Cl attack on C_2H_5OH may not be as clean a source as is the photolysis[3] of $CH_3COCHOHCH_3$.

The temperature dependence of the rate coefficient determined by Grotheer *et al.*[1] shows a marked non-Arrhenius behavior, but this needs to be confirmed before a recommendation can be made.

Evidence for the reaction between CH_3CHOH and O_2 yielding CH_3CHO as a major product comes from the product study of the photooxidation of ethanol by Carter *et al.*[5]

References

[1] H.-H. Grotheer, G. Riekert, D. Walter, and Th. Just, *22nd International Symposium on Combustion, 1988* (Combustion Institute, Pittsburgh, PA 1989), pp. 963–972.

[2] C. Anastasi, V. Simpson, J. Munk, and P. Pagsberg, Chem. Phys. Lett **164**, *18 (1989)*.

[3] A. Miyoshi, H. Matsui, and N. Washida, Chem. Phys. Lett. **160**, 29 (1989).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

[5] W. P. L. Carter, K. R. Darnall, R. A. Graham, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **83**, 2305 (1979).

$CH_2CH_2OH + O_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k = 3.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The direct measurements[1] of this rate coefficient, from the pulsed laser photolysis of either $ClCH_2CH_2OH$ or $BrCH_2CH_2OH$ as the radical source, showed a good level of consistency. By analogy with the reactions $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ and $CH_3CO + O_2 + M \rightarrow CH_3CO_3 + M$ (this evaluation), the rate coefficient for this reaction is expected to be close to the high-pressure limit under the experimental conditions employed. The UV absorption spectrum of the $HOCH_2CH_2O_2$ radical has recently been observed[2,3] by pulsed radiolysis of SF_6-H_2O mixtures[2] and laser flash photolysis of H_2O_2 (Ref. 3) in the presence of C_2H_4 and O_2. These observations indicate that the reaction between CH_2CH_2OH radicals and O_2 leads significantly to the adduct peroxy radical. The preferred value is identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] A. Miyoshi, H. Matsui, and N. Washida, Chem. Phys. Lett. **160**, 29 *(1989)*.

[2] C. Anastasi, D. J. Muir, V. J. Simpson, and P. Pagsberg, J. Phys. Chem **95**, 5791 (1991).

[3] T. P. Murrells, M. E. Jenkin, S. J. Shalliker, and G. D. Hayman, J. Chem Soc. Faraday Trans. **87**, 2351 (1991).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_3O + O_2 \rightarrow HCHO + HO_2$

$\Delta H^\circ = -111.6$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.9 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.2 \times 10^{-14} \exp(-1080/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 298–610 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The direct measurements of the rate coefficients by Lorenz *et al.*[1] (298–450 K) and Wantuck *et al.*[2] (298–973 K) are in good agreement with the similar measurements of Gutma *et al.*[3] (413–608 K), where the temperature ranges overlap The preferred values are derived from a least-mean-square analysis of these three sets of data[1–3] over the temperatur range 298–608 K and are identical to our previous evaluation, IUPAC, 1992.[4] The higher temperature measurement of Wantuck *et al.*[2] give a clear indication of non-Arrheniu behavior over the extended temperature range. The anomalously low *A*-factor for a simple H-atom transfer reaction an the possibility of a more complicated mechanism have bot been noted.[5]

References

[1]K. Lorenz, D. Rhäsa, R. Zellner, and B. Fritz, Ber. Bunsenges. Phys. Chem. 89, 341 (1985).

[2]P. J. Wantuck, R. C. Oldenborg, S. L. Baughcum, and K. R. Winn, J. Phys. Chem. 91, 4653 (1987).

[3]D. Gutman, N. Sanders, and J. E. Butler, J. Phys. Chem. 86, 66 (1982).

[4]IUPAC, Supplement IV, 1992 (see references in Introduction).

[5]NASA Evaluation No. 9, 1990 (see references in Introduction).

$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$

$\Delta H^\circ = -134.0\ kJ \cdot mol^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 9.5 \times 10^{-15}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k = 6.0 \times 10^{-14} \exp(-550/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 295–425 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient and the temperature dependence are obtained from the mean of the room temperature rate coefficients of Gutman *et al.*[1] (296 K) and of Hartmann *et al.*[2] (295 K) and by taking the rounded-off value of *E/R* of Hartmann *et al.*[2] The rate coefficients of Gutman *et al.*[1] and of Hartmann *et al.*[2] differ by 30–50% which, although within the range of the individual error limits, is somewhat higher than might be expected from two direct studies.

The relative rate measurements of Zabarnick and Heicklen[3] are within the error limits which we recommend for our preferred values. We have not taken these results into account, however, owing to the uncertainty concerned with the rate coefficient of the reference reaction of $CH_3O + NO \rightarrow$ products.

It should be noted that the *A*-factor for the above reaction is very low, but in keeping with that for the analogous reaction $CH_3O + O_2 \rightarrow HCHO + HO_2$. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1]D. Gutman, N. Sanders, and J. E. Butler, J. Phys. Chem. 86, 66 (1982).

[2]D. Hartmann, J. Karthäuser, J. P. Sawerysyn, and R. Zellner, Ber. Bunsenges. Phys. Chem. 94, 639 (1990).

[3]S. Zabarnick and J. Heicklen, Int. J. Chem. Kinet. 17, 455 (1985).

[4]IUPAC, Supplement IV, 1992 (see references in Introduction).

$n\text{-}C_3H_7O + O_2 \rightarrow C_2H_5CHO + HO_2$

$\Delta H^\circ = -131.4\ kJ \cdot mol^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 8 \times 10^{-15}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred value is identical to our previous evaluation, IUPAC, 1992.[1] The rate coefficient at 298 K is derived from the study of Zabarnick and Heicklen[2] which, though heavily dependent upon the choice of data for the reference reaction, $n\text{-}C_3H_7O + NO \rightarrow$ products, is consistent with data for other $RO + O_2$ reactions obtained from direct studies. Here we have selected k_{298} to be equal to that for the $C_2H_5O + O_2$ reaction.

The temperature coefficient determined by Zabarnick and Heicklen[2] from their relative rate system is considerably greater than those for the $C_2H_5O + O_2$ (E/R=550 K) or the $i\text{-}C_3H_7O + O_2$ (E/R=200 K) reactions, both of which were obtained from direct studies. This aspect of the reaction requires further experimental work.

References

[1]IUPAC, Supplement IV, 1992 (see references in Introduction).

[2]S. Zabarnick and J. Heicklen, Int. J. Chem Kinet. 17, 477 (1985).

$i\text{-}C_3H_7O + O_2 \rightarrow CH_3COCH_3 + HO_2$

$\Delta H° = -150.3$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.5 \times 10^{-14} \exp(-200/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–390 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.[1] The results of Balla *et al.*[2] on the rate coefficient of this reaction appear reasonable in relation to data for other reactions of this type. Both the rate coefficient and temperature coefficient require confirmation.

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).

[2] R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **99**, 323 (1985).

$R_1(R_2)CHO + O_2 \rightarrow R_1COR_2 + HO_2$ or $\rightarrow$ products (1)

$R_1(R_2)CHO + M \rightarrow R_1CHO + R_2 + M$ (2)

(R=H, alkyl or substituted alkyl)

Rate coefficient data

Reactions	$k_1 \cdot k_2^{-1}$/cm^3 molecule^{-1}	Temp./K	Reference	Comments
$CH_3OCH_2O + O_2 \rightarrow CH_3OCHO + HO_2$ (1) $CH_3OCH_2O + M \rightarrow CH_3OCHO + H + M$ (2)	$k_1[O_2] \sim k_2$ (1 atm, air)	295	Jenkin *et al.*, 1993[1]	(a)
$CH_3COCH_2O + O_2 \rightarrow CH_3COCHO + HO_2$ (1)	$k_1[O_2] \ll k_2$ (1 atm, air)	298	Jenkin *et al.*, 1993[2]	(b)
$CH_3COCH_2O + M \rightarrow CH_3CO + HCHO + M$ (2)	$k_1[O_2] \ll k_2$ (1 atm, air)	298	Bridier *et al.*, 1993[3]	(c)

Comments

(a) Steady-state photolyses of Cl_2-CH_3OCH_3-O_2-N_2 mixtures (10–760 Torr) with long-path FTIR analyses, and molecular modulation studies of similar reactant mixtures with UV absorption monitoring of $CH_3OCH_2O_2$ radicals. In both systems, kinetic treatments indicate that reactions (1) and (2) were competing under the conditions of the experiments.

(b) Steady-state photolyses of Cl_2-CH_3COCH_3-O_2-N_2 mixtures (700 Torr) with long-path FTIR and long-path UV visible diode array spectroscopy analyses of products. Data indicate that reaction (2) predominated over reaction (1) under the conditions of the experiments.

(c) Flash photolyses of Cl_2-CH_3COCH_3-air mixtures (1 atm) with UV absorption monitoring of $CH_3COCH_2O_2$ radicals. Data indicate that reaction (2) predominated over reaction (1) under the conditions of the experiments.

Preferred Values

No quantitative recommendations.

Comments on Preferred Values

Although the results listed above for the reactions of the CH_3OCH_2O and CH_3COCH_2O radicals are not quantitative, for the purposes of atmospheric modeling studies it is recommended that the above qualitative information on the ratios k_1/k_2 be used to decide if one or the other of the alkoxy radical reaction pathways predominates, or if both pathways should be considered.

References

[1] M. E. Jenkin, G. D. Hayman, T. J. Wallington, M. D. Hurley, J. C. Ball, O. J. Nielsen, and T. Ellermann, J. Phys. Chem. **97**, 11712 (1993).

[2] M. E. Jenkin, R. A. Cox, M. Emrich, and G. K. Moortgat, J. Chem. Soc. Faraday Trans. **89**, 2983 (1993).

[3] I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. **89**, 2993 (1993).

$CH_3 + O_3 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k = 2.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.1 \times 10^{-12} \exp(-210/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–400 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values are based on the revised calculations by Paltenghi *et al.*[1] of the earlier data of Ogryzlo *et al.*,[2] which result from a correction for the pressure drop along the flow tube between the reaction vessel and the manometer, and are identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] R. Paltenghi, E. A. Ogryzlo, and K. D. Bayes, J. Phys. Chem. **88**, 2595 (1984).
[2] E. A. Ogryzlo, R. Paltenghi, and K. D. Bayes, Int. J. Chem. Kinet. **13**, 667 (1981).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_3O + NO + M \rightarrow CH_3ONO + M$ (1)

$CH_3O + NO \rightarrow HCHO + HNO$ (2)

$\Delta H^\circ(1) = -173.2$ kJ·mol^{-1}
$\Delta H^\circ(2) = -116.9$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.6 \pm 1.3) \times 10^{-30}$ [He]	296	Ohmori, Yamasaki, and Matsui, 1993[1]	(a)
$(4.3 \pm 1.0) \times 10^{-30}$ [N_2]	296		
$(1.01 \pm 0.45) \times 10^{-29}$ [CF_4]	296		
$(1.55 \pm 0.40) \times 10^{-29}$ [SF_6]	296		
Reviews and Evaluations			
$1.6 \times 10^{-29} (T/300)^{-3.5}$ [N_2]	200–400	IUPAC, 1992[2]	(b)
$1.4 \times 10^{-29} (T/300)^{-3.8}$ [Air]	200–300	NASA, 1994[3]	(c)

Comments

(a) CH_3O radicals were generated by photolysis of CH_3ONO at 266 and 355 nm and detected by LIF. Bath gas pressures were varied between 7–100 Torr (He), 10–70 Torr (N_2), 15–50 Torr (CF_4), and 10–50 Torr (SF_6).

(b) Based on the data of Refs. 4 and 5 using $F_c = 0.6$. A branching ratio of $k_2/(k_1 + k_2) = 0.45$ is reported in Ref. 6.

(c) Taken from the results of Frost and Smith[4] for M = Ar.

Preferred Values

$k_{01} = 1.6 \times 10^{-29} (T/300)^{-3.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

$k_2 = 4 \times 10^{-12} (T/300)^{-0.7}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability
$\Delta \log k_{01} = \pm 0.1$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred rate coefficient values are based on the data of Frost and Smith[4] and McCaulley *et al.*,[5] and are identical to our previous evaluation, IUPAC, 1992.[2] The branching ratio is also from Ref. 2. The recently reported k_{01} values by Ohmori *et al.*[1] forM=N_2 at 296 K are a factor of 3.7 lower than previously recommended. The cause of this difference is not clear but it may be in the separation of k_1 and k_2.

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comment
Absolute Rate Coefficients			
$(4.5\pm1.5)\times10^{-11}$	298	Ohmori, Yamasaki, and Matsui, 1993[1]	(a)
Reviews and Evaluations			
3.6×10^{-11} $(T/300)^{-0.6}$	200–400	IUPAC, 1992[2]	(b)
3.6×10^{-11} $(T/300)^{-0.6}$	200–300	NASA, 1994[3]	(c)

Comments

(a) See comment (a) for k_{01}. $k_{\infty 1}$ evaluated using Lindemann-Hinshelwood theory, i.e., using $F_c=1$.

(b) The recommended values are from Ref. 4. Because they have been evaluated with $F_c=1$, an increase of $k_{\infty 1}$ is expected when an analysis with a smaller, more realistic value of F_c is done.

(c) See comment (c) for k_{01}.

Preferred Values

$k_{\infty 1}=3.6\times10^{-11}(T/300)^{-0.6}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta\log k_{\infty 1}=\pm0.5$ at 298 K.

$\Delta n=\pm0.5$.

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992,[2] and are consistent with the results from Ohmori *et al.*[1] at 296 K.

References

[1] K. Ohmori, K. Yamasaki, and H. Matsui, Bull. Chem. Soc. Jpn. **66**, 51 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 175 (1990).

[5] J. A. McCaulley, A. M. Moyle, M. F. Golde, S. M. Anderson, and Kaufman, J. Chem. Soc. Faraday Trans. **86**, 4001 (1990).

[6] M. E. Jenkin, G. D. Hayman, and R. A. Cox, J. Photochem. A **42**, 18 (1988).

$C_2H_5O + NO + M \rightarrow C_2H_5ONO + M$ (1)
$C_2H_5O + NO \rightarrow CH_3CHO + HNO$ (2)

$\Delta H^\circ(1)=-176.9$ kJ·mol^{-1}
$\Delta H^\circ(2)=-139.3$ kJ·mol^{-1}

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty 1}=4.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

$k_2=1.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 300 K.

Reliability

$\Delta\log k_{\infty 1}=\pm0.3$ at 298 K.

$\Delta n=\pm0.5$.

Comments on Preferred Values

The recommended value of $k_{\infty 1}$ is based on the data of Frost and Smith,[1] and is consistent with values for related reactions such as $CH_3O + NO + M \rightarrow CH_3ONO + M$ and $i\text{-}C_3H_7O + NO + M \rightarrow i\text{-}C_3H_7ONO + M$ (see this evaluation). The value of k_2 is estimated via the preferred value of $k_{\infty 1}$ and the ratio $k_2/k_{\infty 1}=0.3$ such as measured in Ref. 2. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1757 (1990).

[2] G. Baker and R. Shaw, J. Chem. Soc. A, 6965 (1965).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$i\text{-}C_3H_7O + NO + M \rightarrow i\text{-}C_3H_7ONO + M$ (1)
$i\text{-}C_3H_7O + NO \rightarrow (CH_3)_2CO + HNO$ (2)

$H^\circ(2)=-155.6$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty 1}=3.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

$k_2=6.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 300 K.

Reliability

$\Delta\log k_{\infty 1}=\pm0.3$ at 298 K.

$\Delta n=\pm0.5$.

$\Delta\log k_2=\pm0.5$ at 298 K.

Comments on Preferred Values

The preferred value of $k_{\infty 1}$ is based on the study of Balla *et al.*,[1] and is identical to our previous evaluation, IUPAC, 1992.[2] The value of k_2 is obtained from the preferred $k_{\infty 1}$ and the rate coefficient ratio $k_2/k_1=0.19\pm0.03$, independent of temperature, measured in Ref. 3.

References

[1] R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **99**, 323 (1985).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] L. Batt and R. T. Milne, Int. J. Chem. Kinet. **9**, 141 (1977).

$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M$ (1)
$CH_3O + NO_2 \rightarrow HCHO + HONO$ (2)

$H^\circ(1)=-170.5$ kJ·mol^{-1}

$H^\circ(2)=-238.9$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{01}=2.8\times10^{-29}\ (T/300)^{-4.5}\ [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta\log k_{01}=\pm0.3$ at 298 K.

$\Delta n=\pm1$.

Comments on Preferred Values

The agreement between the studies of Refs. 1 and 2 appears satisfactory, in particular if the different ways of treating the falloff curve are taken into account. We assume similar values of k_0 for M=Ar and N_2. Falloff curves are constructed with $F_c=0.44$ at 300 K such as chosen in Ref. 2. Reaction (2) appears to play only a minor role at pressures above 10 Torr.[1]

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty 1}=2.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta\log k_{\infty 1}=\pm0.3$ at 298 K.

$\Delta n=\pm0.5$.

Comments on Preferred Values

The preferred $k_{\infty 1}$ value based on Ref. 2 appears consistent with the values for related reactions RO + NO + M

$\rightarrow$ RONO + M (with R = CH_3, C_2H_5, i-C_3H_7, see this evaluation). Falloff curves are constructed with F_c=0.44 from Ref. 2. Reaction (2) appears to be only of minor importance.[1] These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] J. A. McCaulley, S. M. Anderson, J. B. Jeffries, and F. Kaufman, Chem. Phys. Lett. **115**, 180 (1985).

[2] M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 17 (1990).

[3] IUPAC, Supplement [illegible] in Introduction).

$C_2H_5O + NO_2 + M \rightarrow C_2H_5ONO_2 + M$ (1)
$C_2H_5O + NO_2 \rightarrow CH_3CHO + HONO$ (2)

$\Delta H°(1) = -170.0$ kJ·mol^{-1}
$\Delta H°(2) = -261.3$ kJ·mol^{-1}

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty 1} = 2.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The value of $k_{\infty 1}$ is based on the data of Frost and Smith,[1] and appears consistent with values for related reactions[2] such as RO + NO + M $\rightarrow$ RONO + M (with M = CH_3, C_2H_5, and i-C_3H_7) or $CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M$ (see this evaluation). Reaction (2) appears to be of minor importance ($k_2/k_{\infty 1} < 0.2$) in the high-pressure range of the reaction[2] (see also the $CH_3O + NO_2$ reaction system; this evaluation). The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1751 (1990).

[2] R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

i-$C_3H_7O + NO_2 + M \rightarrow i$-$C_3H_7ONO_2 + M$ (1)
i-$C_3H_7O + NO_2 \rightarrow (CH_3)_2CO + HONO$ (2)

$\Delta H°(1) = -171.7$ kJ·mol^{-1}
$\Delta H°(2) = -277.6$ kJ·mol^{-1}

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty 1} = 3.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

This recommendation is based on Ref. 1. The values of $k_{\infty 1}$ are consistent with other related reactions such as RO + NO + M $\rightarrow$ RONO + M and RO + NO_2 + M $\rightarrow$ $RONO_2$+ M (with R = CH_3, C_2H_5, i-C_3H_7, see this evaluation and Ref. 2). It is estimated that $k_2/k_{\infty 1} < 0.2$. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **99**, 323 (1985).

[2] R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

$\Delta H^\circ = -49.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
([illegible]1.4)$\times 10^{-12}$	298	Sehested, Nielsen, and Wallington, 1993[1]	(a)
Reviews and Evaluations			
[illegible]$\times 10^{-12}$ exp(200/T)	240–370	Wallington, Dagaut, and Kurylo, 1992[2]	(b)
4.2$\times 10^{-12}$ exp(180/T)	218–365	Lightfoot *et al.*, 1992[3]	(c)
4.2$\times 10^{-12}$ exp(180/T)	240–360	IUPAC, 1992[4]	(c)
4.2$\times 10^{-12}$ exp(180/T)	200–300	NASA, 1994[5]	(c)

Comments

(a) Pulse radiolysis of SF_6-CH_4-O_2-NO mixtures at a total pressure of 760 Torr, with UV absorption determination of $[CH_3O_2]$.

(b) Least-squares analysis of selected data of Plumb *et al.*,[6,7] Cox and Tyndall,[8] Sander and Watson,[9] Ravishankara *et al.*,[10] Simonaitis and Heicklen,[11] and Zellner *et al.*[12]

(c) k_{298} was the mean of the data of Plumb *et al.*,[7] Cox and Tyndall,[8] Sander and Watson,[9] Ravishankara *et al.*,[10] Simonaitis and Heicklen,[11] and Zellner *et al.*,[12] and E/R was from the data of Ravishankara *et al.*[10] and Simonaitis and Heicklen.[11]

Preferred Values

$k = 7.6\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.2\times 10^{-12}$ exp(180/T) cm^3 molecule^{-1} s^{-1} over the temperature range 240–360 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 180$ K.

Comments on Preferred Values

The data of Sehested *et al.*[1] are in good agreement with the earlier results,[6–12] and the preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] J. Sehested, O. J. Nielsen, and T. J. Wallington, Chem. Phys. Lett. **213**, 457 (1993).
[2] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).
[3] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).
[5] NASA Evaluation No. 11, 1994 (see references in Introduction).
[6] I. C. Plumb, K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, Chem. Phys. Lett. **63**, 255 (1979).
[7] I. C. Plumb, K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, J. Phys. Chem. **85**, 3136 (1981).
[8] R. A. Cox and G. Tyndall, Chem. Phys. Lett. **65**, 357 (1979); J. Chem. Soc. Faraday Trans. 2, **76**, 153 (1980).
[9] S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).
[10] A. R. Ravishankara, F. L. Eisele, N. M. Kreutter, and P. H. Wine, J. Chem. Phys. **74**, 2267 (1981).
[11] R. Simonaitis and J. Heicklen, J. Phys. Chem. **85**, 2946 (1981).
[12] R. Zellner, B. Fritz, and K. Lorenz, J. Atmos. Chem. **4**, 241 (1986).

$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$ (1)

$C_2H_5O_2 + NO + M \rightarrow C_2H_5ONO_2 + M$ (2)

$\Delta H^\circ(1) = -45.6\ kJ \cdot mol^{-1}$
$\Delta H^\circ(2) = -215.6\ kJ \cdot mol^{-1}$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comment
Absolute Rate Coefficients			
$(8.5 \pm 1.2) \times 10^{-12}$	298	Sehested, Nielsen, and Wallington, 1993[1]	(a)
Reviews and Evaluations			
9×10^{-12}	298	Wallington, Dagaut, and Kurylo, 1992[2]	(b)
8.9×10^{-12}	298	Lightfoot *et al.*, 1992[3]	(b)
8.9×10^{-12}	298	IUPAC, 1992[4]	(b)
$k_2/k \leq 0.014$ (1 bar)	298		(c)
8.7×10^{-12}	200–300	NASA, 1994[5]	(d)

Comments

(a) Pulse radiolysis study of SF_6-C_2H_6-O_2-NO mixtures at a total pressure of 760 Torr, with UV absorption kinetic spectroscopy of $C_2H_5O_2$ radicals.

(b) Based on the data of Plumb *et al.*[6]

(c) Based on the data of Atkinson *et al.*[7]

(d) Based on the room temperature rate coefficients of Plumb *et al.*[6] and Sehested *et al.*[1] The zero temperature dependence of the rate coefficient was estimated.

Preferred Values

$k = 8.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k \leq 0.014$ at 298 K and 1 bar pressure.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred value of k_{298} is the mean of the data of Plumb *et al.*[6] and Sehested *et al.*,[1] which are in excellent agreement. A measurement of the temperature dependence of k is still lacking but it appears likely that *E/R* will be close to zero by analogy with the CH_3O_2 + NO reaction.

References

[1] J. Sehested, O. J. Nielsen, and T. J. Wallington, Chem. Phys. Lett. **213**, 457 (1993).
[2] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).
[3] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).
[5] NASA Evaluation No. 11, 1994 (see references in Introduction).
[6] I. C. Plumb, K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, Int. J. Chem Kinet. **14**, 183 (1982).
[7] R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **86**, 4563 (1982).

$HOCH_2CH_2O_2 + NO \rightarrow HOCH_2CH_2O + NO_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9 \pm 4) \times 10^{-12}$	298	Becker, Geiger, and Wiesen, 1991[1]	(a)
Reviews and Evaluations			
9×10^{-12}	298	Lightfoot *et al.*, 1992[2]	(b)

Comments

(a) Pulsed excimer laser photolysis of H_2O_2 in the presence of C_2H_4-O_2-NO mixtures at total pressures of 760 ± 5 Torr. Relative HO radical concentrations were determined as a function of time using LIF, and simulated by a mechanism consisting of 11 reactions, of which k of above reaction was the most sensitive.

(b) Based on the data of Becker *et al.*[1]

Preferred Values

$k=$[illegible]0×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.5$ at 298 K.

Comments on Preferred Values

The rate coefficient reported by Becker *et al.*,[1] which is recommended, is consistent with the rate coefficients of the reactions of CH_3O_2 and $C_2H_5O_2$ radicals with NO. Independent confirmation is needed to reduce the recommended error limits.

References

[1] K. H. Becker, H. Geiger, and P. Wiesen, Chem. Phys. Lett. **184**, 256 (1991).

[2] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).

$n\text{-}C_3H_7O_2 + NO \rightarrow n\text{-}C_3H_7O + NO_2$ (1)
$n\text{-}C_3H_7O_2 + NO + M \rightarrow n\text{-}C_3H_7ONO_2 + M$ (2)

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2$)

$k=5.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k=0.020$ at 298 K and 1 bar pressure.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(k_2/k)=\pm0.01$ at 298 K (1 bar).

Comments on Preferred Values

In our previous evaluations,[1-3] in the absence of any experimental data we recommended the value $k=8.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K by analogy with the reaction $C_2H_5O_2$ + NO → products and in line with our recommendations for the reaction $i\text{-}C_3H_7O_2$ + NO → products. Now that we have changed the recommendation for the latter reaction, we have also changed the above recommendation, but note that it is still in line with the value for the reaction, $C_2H_5O_2$ + NO → products.

The preferred branching ratio is that measured by Atkinson *et al.*[4] and subsequently revised by Carter and Atkinson.[5]

References

[1] CODATA, Supplement II, 1984 (see references in Introduction).

[2] IUPAC, Supplement III, 1989 (see references in Introduction).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **86**, 4563 (1982).

[5] W. P. L. Carter and R. Atkinson, J. Atmos. Chem. **8**, 165 (1989).

$i\text{-}C_3H_7O_2 + NO \rightarrow i\text{-}C_3H_7O + NO_2$ (1)

$i\text{-}C_3H_7O_2 + NO + M \rightarrow i\text{-}C_3H_7ONO_2 + M$ (2)

$\Delta H^\circ(1)=-40.5$ kJ·mol^{-1}
$\Delta H^\circ(2)=-212.2$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.0\pm1.2)\times10^{-12}$	290	Peeters, Vertommen, and Langhans, 1992[1]	(a)
Branching Ratios			
$k_2/k=0.042\pm0.003$ (735 Torr air)	299	Atkinson *et al.*, 1982[2]; Carter and Atkinson, 1989[3]	(b)
Reviews and Evaluations			
8.9×10^{-12}	298	IUPAC, 1992[4]	(c)
$k_2/k=0.043$	298		
4.3×10^{-12}	294	Lightfoot *et al.*, 1992[5]	(d)

Comments

(a) Fast-flow system with molecular beam sampling mass spectrometry at a total pressure of 2 Torr. The rate coefficient k was derived from the rate of formation of NO_2.

(b) Photolysis of CH_3ONO-NO-C_3H_8 or Cl_2-NO-C_3H_8 mixtures at total pressures of 735 Torr of air. The branching ratio was determined[2] from the measured yields of i-$C_3H_7ONO_2$ and the consumption of C_3H_8. Carter and Atkinson[3] have recalculated the branching ratio, cited above, from the original data[2] on the basis of revised data for the rate coefficients of the HO + alkane reactions.

(c) The value of k was assumed to be equal to that of the reaction of $C_2H_5O_2$ + NO → products, and the branching ratio was taken from Atkinson *et al.*[2]

(d) Average of the data of Adachi and Basco[6] and Peeters *et al.*[1]

Preferred Values

$k=5.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2/k=0.042$ at 298 K and 1 bar pressure.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

$\Delta(k_2/k)=\pm0.01$ at 298 K (1 bar).

Comments on Preferred Values

The recent study of Peeters *et al.*[1] appears to be reliable and their rate coefficient is recommended. The earlier result of Adachi and Basco[6] ($k=3.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K), although now reasonably close to our recommended value, was discounted in our previous evaluation.[4]

References

[1] J. Peeters, J. Vertommen, and I. Langhans, Ber. Bunsenges. Phys. Chem. **96**, 431 (1992).

[2] R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **86**, 4563 (1982).

[3] W. P. L. Carter and R. Atkinson, J. Atmos. Chem. **8**, 165 (1989).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

[5] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 180 (1992).

[6] H. Adachi and N. Basco, Int. J. Chem. Kinet. **14**, 1243 (1982).

$CH_3CO_3 + NO \rightarrow CH_3 + CO_2 + NO_2$

$\Delta H^\circ=-133$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=2.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 280–325 K.

Reliability

$\Delta\log k=\pm0.2$ over the temperature range 280–325 K.

$\Delta(E/R)=\pm600$ K.

Comments on Preferred Values

The two studies[1,2] of the rate coefficient ratio $k/k(CH_3CO_3 + NO_2)$ are in good agreement. The preferred value is obtained from the mean value of $k/k(CH_3CO_3 + NO_2)=2.1\pm0.3$ obtained from the data of Kirchner *et al.*[1] and Tuazon *et al.*[2] at total pressures of 740 and 750 Torr of air. Over the temperature range 283–321 K these two sets of data indicate that this ratio is essentially temperature-independent, within the error limits of the measurements (E/R $=646\pm$ 564 K). The rate coefficient k was then obtained by taking $k(CH_3CO_3+NO_2)=9.3\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 1 atm pressure (see data sheets for the reaction $CH_3CO_3 + NO_2 + M \rightarrow CH_3CO_3 + NO_2 + M$, this evaluation). The preferred values are identical to our previous evaluation, IUPAC, 1992.[3]

The experiments of Kirchner *et al.*[1] also show that the rate coefficient k shows no pressure dependence over the pressure range 22–750 Torr, as expected.

References

[1] F. Kirchner, F. Zabel, and K. H. Becker, Ber. Bunsenges. Phys. Chem. **94**, 1379 (1990).

[2] E. C. Tuazon, W. P. L. Carter, and R. Atkinson, J. Phys. Chem. **95**, 2434 (1991).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$C_2H_5CO_3 + NO \rightarrow C_2H_5 + CO_2 + NO_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
1.9×10^{-11}	302	Kerr and Stocker, 1985[1]	(a)

Comments

(a) Photolysis of dilute mixtures of synthetic air containing NO, NO_2, and C_2H_5CHO at a total pressure of 1 atm. The rate coefficient ratio $k/k(C_2H_5CO_3 + NO_2) = 1.9$ was determined from the effect of the $[NO]/[NO_2]$ ratio on the yield of peroxypropionyl nitrate, $CH_3CH_2C(O)OONO_2$. The rate coefficient k is calculated here using a rate coefficient of $k(C_2H_5CO_3 + NO_2) = 1.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 atm pressure, by analogy with the reaction $CH_3CO_3 + NO_2 + M$ (this evaluation).

Preferred Values

$k = 2.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

This reaction requires to be studied by a more direct technique to lower the recommended error limits, although the above value is in agreement with the value of $k(CH_3CO_3 + NO) = 2.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 280–325 K (this evaluation).

References

[1] J. A. Kerr and D. W. Stocker, J. Photochem. **28**, 475 (1985).

$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$

$\Delta H^\circ = -88$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 2.5\times10^{-30}\,(T/300)^{-5.5}\,[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the theoretical analysis of Ref. 1, which used the previous experimental determinations. These values are based on a theoretically determined value of $F_c = 0.36$ at 300 K. The difference between Refs. 2 and 3 is due to the different values of F_c used, with the analysis of Ref. 3 being based on a standard value of $F_c = 0.6$. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–350 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

See comments on k_0.

Intermediate falloff range

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	P/Torr	M	Temp./K	Reference	Comment
Relative Rate Coefficients					
$(4.4 \pm 0.4) \times 10^{-12}$	760	air	298	Bridier, Lesclaux, and Veyret, 1992[5]	(a)
$(2.84 \pm 0.15) \times 10^{-12}$	760	air	333		
$(2.25 \pm 0.32) \times 10^{-12}$	760	air	353		
$(2.09 \pm 0.9) \times 10^{-12}$	760	air	368		
$(1.4 \pm 0.4) \times 10^{-12}$	760	air	373		

Comments

(a) Flash photolysis study of the $CH_3O_2 + NO_2 + M \rightleftarrows CH_3O_2NO_2 + M$ reaction system. CH_3 radicals were generated by photolysis of Cl_2-CH_4-O_2 mixtures and monitored at 245 nm. The spectrum of $CH_3O_2NO_2$ was monitored between 200–280 nm. From the temperature dependence of the determined equilibrium constant, $\Delta H^\circ_{298} = -(92.7 \pm 0.5)$ kJ mol^{-1} was derived.

References

[1] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[2] CODATA, Supplement I, 1982 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).
[5] I. Bridier, R. Lesclaux, and B. Veyret, Chem. Phys. Lett. **191**, 259 (1992).

$CH_3O_2NO_2 + M \rightarrow CH_3O_2 + NO_2 + M$

$\Delta H^\circ = 88$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 6.8 \times 10^{-19}$ [N_2] s^{-1} at 298 K.
$k_0 = 9 \times 10^{-5} \exp(-9690/T)$ [N_2] s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values correspond to the data and analysis of Ref. 1. A theoretical analysis of these data and those of the reverse reaction in Ref. 2 gives an internally consistent picture (with $\Delta H^\circ = 88.5$ kJ mol^{-1}). Slightly lower limiting rate coefficients were obtained in Ref. 3, where a value of $F_c = 0.6$ was used. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 4.5\ \mathrm{s}^{-1}$ at 298 K.
$k_\infty = 1.1\times10^{16}\exp(-10560/T)\ \mathrm{s}^{-1}$ over the temperature range 250–300 K.

Reliability
$\Delta\log k_\infty = \pm0.3$ at 298 K.
$\Delta(E/R) = \pm500$ K.

Comments on Preferred Values
See comments on preferred values of k_0.

Intermediate falloff range

Rate coefficient data

[illegible]	P/Torr	M	Temp./K	Reference	Comments
Relative Rate Coefficients					
[illegible] ± 13.2	760	air	333	Bridier, Lesclaux, and Veyret, 1992[5]	(a)
[illegible] ± 34	760	air	353		
[illegible] ± 76	760	air	368		
[illegible] ± 283	760	air	373		

Comments

(a) Flash photolysis study of the $CH_3O_2 + NO_2 + M \rightleftharpoons CH_3O_2NO_2 + M$ reaction system. CH_3O_2 radicals were generated by photolysis of Cl_2-CH_4-O_2 mixtures and monitored at 245 nm. The spectrum of $CH_3O_2NO_2$ was observed between 200–280 nm. From the temperature dependence of the determined equilibrium constant $\Delta H^\circ_{298} = -(92.7\pm0.5)$ kJ mol^{-1} was derived.

References

[1] F. Zabel, A. Reimer, K. H. Becker, and E. H. Fink, J. Phys. Chem. **93**, 5500 (1989).
[2] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[3] A. Bahta, R. Simonaitis, and J. Heicklen, J. Phys. Chem. **86**, 1849 (1982).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).
[5] I. Bridier, R. Lesclaux, and B. Veyret, Chem. Phys. Lett. **191**, 259 (1992).

$C_2H_5O_2 + NO_2 + M \rightarrow C_2H_5O_2NO_2 + M$

$\Delta H^\circ = -67.7\ \mathrm{kJ\cdot mol^{-1}}$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.3\times10^{-29}\,(T/300)^{-6.2}\,[N_2]\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ over the temperature range 200–300 K.

Reliability
$\Delta\log k_0 = \pm0.3$ at 298 K.
$\Delta n = \pm1$.

Comments on Preferred Values

The preferred values are an average of the data from Refs. 1 and 2. The temperature dependence is from the theoretical analysis of Ref. 2. Falloff extrapolations were made with $F_c = 0.31$ at 250–300 K such as given from the theoretical analysis of Ref. 2.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 8.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

See comments on k_0. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992

References

[1] G. Elfers, F. Zabel, and K. H. Becker, Chem. Phys. Lett. **168**, 14 (1990)
[2] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$C_2H_5O_2NO_2 + M \rightarrow C_2H_5O_2 + NO_2 + M$

$\Delta H° = 67.7$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.4 \times 10^{-17}$ [N$_2$] s^{-1} at 298 K.

$k_0 = 4.8 \times 10^{-4} \exp(-9285/T)$ [N$_2$] s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 300 K.
$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values

The dissociation data are consistent with experimental recombination data (see this evaluation) and the theoretical analysis from Ref. 1. Falloff curves are constructed with $F_c = 0.31$ (over the range 250–300 K).

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 5.4$ s^{-1} at 298 K.

$k_\infty = 8.8 \times 10^{15} \exp(-10440/T)$ s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 300 K.
$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values

See comment on k_0. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.[2]

References

[1] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_3CO_3 + NO_2 + M \rightarrow CH_3CO_3NO_2 + M$

$\Delta H° = -119$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 2.7\times10^{-28} (T/300)^{-7.1} [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta\log k_0 = \pm0.4$ at 298 K.

$\Delta n = \pm2$.

Comments on Preferred Values

The extensive and internally consistent study of $CH_3CO_3NO_2$ (PAN) formation and dissociation in Ref. 1 is preferred. Falloff extrapolations were performed with a modeled value of $F_c=0.3$.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 1.2\times10^{-11} (T/300)^{-0.9}$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta\log k_\infty = \pm0.2$ at 298 K.

$\Delta n = \pm1$.

Comments on Preferred Values

See comments on k_0. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.[2]

References

[1] I. Bridier, F. Caralp, H. Loirat, R. Lesclaux, B. Veyret, K. H. Becker, A. Reimer, and F. Zabel, J. Phys. Chem. 95, 3594 (1991).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_3CO_3NO_2 + M \rightarrow CH_3CO_3 + NO_2 + M$

$\Delta H^\circ = 119$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.1\times10^{-20} [N_2]$ s^{-1} at 298 K.

$k_0 = 4.9\times10^{-3} \exp(-12100/T) [N_2]$ s^{-1} over the temperature range 300–330 K.

Reliability

$\Delta\log k_0 = \pm0.4$ at 298 K.

$\Delta(E/R) = \pm1000$ K.

Comments on Preferred Values

The data base of Ref. 1 is large enough to allow for a falloff extrapolation to k_0, in part because falloff curves for PAN dissociation and recombination were measured independently. Falloff extrapolations were made with a modeled value of $F_c=0.3$. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[2]

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.5\times10^{17} \exp[-(14340\pm250)/T]$	302–323	Roberts and Bertman, 1992[3]	(a)
3.1×10^{-4}	298	Rouwelis and Glavas, 1992[4]	(b)
$1.6\times10^{16} \exp[-(13539\pm1060)/T]$	288–298	Grosjean, Grosjean, and Williams, 1992[5]	(c)
Reviews and Evaluations			
$4.0\times10^{16} \exp(-13600/T)$	298–330	IUPAC, 1992[2]	(d)

Comments

(a) Thermal decomposition of PAN at 760 Torr total pressure. PAN concentrations were measured by packed column GC with electron capture detection.

(b) Thermal decomposition of PAN in N_2 as well in the presence of O_2, NO_2, and NO at 1 atm total pressure. The products methyl nitrate and NO_2 in pure PAN-N_2 mixtures were measured by GC. In the presence of large amounts of O_2, no methyl nitrate was formed at 333 K, indicating that the decomposition of PAN to methyl nitrate and CO_2 does not occur. The data obtained were simulated with 23 reactions.

(c) Thermal decomposition of PAN in 1 atm of air. PAN was measured by GC with electron capture detection.

(d) Based on the rate data of Refs. 1 and 6 at 1 atm total pressure.

Preferred Values

$k_\infty=3.8\times10^{-4}\ s^{-1}$ at 298 K.

$k_\infty=5.4\times10^{16}\ \exp(-13830/T)\ s^{-1}$ over the temperature range 300–330 K.

Reliability

$\Delta\log k_\infty=\pm0.3$ at 298 K.

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The recently reported values from Refs. 3–5 are in very good agreement at 298 K but are a factor of two smaller than our previous recommendation.[2] The preferred values attempt to reconcile all measurements. The direct PAN decompositions to methyl nitrate and CO_2[4,7] or to CH_3CO_2 and NO_3[7] are very slow compared to the decomposition to $CH_3CO_3 + NO_2$.

References

[1] I. Bridier, F. Caralp, H. Loirat, R. Lesclaux, B. Veyret, K. H. Becker, A. Reimer, and F. Zabel, J. Phys. Chem. **95**, 3594 (1991).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] J. M. Roberts and S. B. Bertman, Int. J. Chem. Kinet. **24**, 297 (1992).

[4] N. Roumelis and S. Glavas, Monatsch. Chem. **123**, 63 (1992).

[5] D. Grosjean, E. Grosjean, and E. L. Williams II, Air & Waste **44**, 391 (1994).

[6] E. C. Tuazon, W. P. L. Carter, and R. Atkinson, J. Phys. Chem. **95**, 2434 (1991).

[7] J. J. Orlando, G. S. Tyndall, and J. G. Calvert, Atmos. Environ. **26A**, 3111 (1992).

$C_2H_5CO_3NO_2 + M \rightarrow C_2H_5CO_3 + NO_2 + M$

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2\times10^{15}\ \exp(-12800/T)$	298–315	Mineshos and Glavas, 1991[1]	(a)

Comments

(a) Thermal decomposition of peroxypropionyl nitrate (PPN) in a 4.5 liter glass flask in the presence of 1 atm N_2. PPN and the products, ethyl nitrate, NO_2, and methyl nitrate, were analyzed by GC at 323 K. In the presence of NO, ethyl nitrate was the major product observed.[1]

Preferred Values

$k_\infty=4.4\times10^{-4}\ s^{-1}$ at 298 K.

$k_\infty=2\times10^{15}\ \exp(-12800/T)\ s^{-1}$ over the temperature range 300–315 K.

Reliability

$\Delta\log k_\infty=\pm0.4$ at 298 K.

$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The values from the only reported study of this reaction by Mineshos and Glavas[1] are recommended here.

References

[1] G. Mineshos and S. Glavas, React. Kinet. Catal. Lett. **45**, 305 (1991).

$CH_3O_2 + NO_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.3\pm0.7)\times10^{-12}$	298	Crowley *et al.*, 1990[1]	(a)

Comments

(a) Molecular modulation study involving the 253.7 nm photolysis of HNO_3-CH_4-O_2 mixtures in a flow system. The rate coefficient k was derived from a computer fit of the NO_3 radical absorption profiles (at 623 nm) based on a mechanism of 33 reactions.

Preferred Values

No recommendation.

Comments on Preferred Values

The only reported study of this reaction by Crowley *et al.*[1] involves a complex system of chemical reactions and consequently leads to a very indirect determination of the rate coefficient. Until more work is carried out on this reaction, we make no recommendation.

A further study by Crowley *et al.*,[2] using HNO_3 as a source of NO_3 radicals, has shown that an additional "dark" source of NO_3 radicals arises from the thermal decomposition of N_2O_5, present in the initial HNO_3. Taking this into account[2] may reduce the rate coefficient reported above[1] by as much as a factor of 3.

References

[1] J. N. Crowley, J. P. Burrows, G. K. Moortgat, G. Poulet, and G. Le Bras, Int. J. Chem. Kinet. 22, 673 (1990).

[2] J. N. Crowley, J. P. Burrows, G. K. Moortgat, G. Poulet, and G. Le Bras, Int. J. Chem. Kinet. 25, 795 (1993).

$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2$ (1)
$\rightarrow 2CH_3O + O_2$ (2)
$\rightarrow CH_3OOCH_3 + O_2$ (3)

$\Delta H^\circ(1) = -331.0$ kJ·mol^{-1}
$\Delta H^\circ(2) = 14.4$ kJ·mol^{-1}
$\Delta H^\circ(3) = -146.5$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2+k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.0\times10^{-13}\exp(416/T)$	248–700	Lightfoot *et al.*, 1991[1]	(a,b)
Reviews and Evaluations			
$1.1\times10^{-13}\exp(365/T)$	200–400	IUPAC, 1992[2]	(c)
$9.2\times10^{-14}\exp(390/T)$	250–600	Wallington, Dagaut, and Kurylo, 1992[3]	(d)
$9.1\times10^{-14}\exp(416/T)$	248–650	Lightfoot *et al.*, 1992[4]	(e)
$2.5\times10^{-13}\exp(190/T)$	200–300	NASA, 1994[5]	(f)

Comments

(a) k is defined by $-d[CH_3O_2]/dt = 2k[CH_3O_2]^2$ and was derived from the measured overall second-order decay of CH_3O_2 radicals (k_{obs}) by correcting for secondary removal of CH_3O_2 radicals.

(b) Flash photolysis-UV absorption study of Cl_2-CH_3OH-CH_4-O_2-N_2 mixtures at 760 Torr over the temperature range 600–719 K. The temperature-dependent value of k listed above was derived by the authors from a re-analysis of all of their data, including previous studies, from flash photolysis experiments.

(c) See Comments on Preferred Values.

(d) $k_{obs} = 2.5\times10^{-13}\exp(180/T)$ cm^3 molecule^{-1} s^{-1} was derived from a least-squares analysis of the data of Anastasi *et al.*,[6] Sander and Watson,[7] Kurylo and Wallington,[8] Lightfoot *et al.*,[9] and Jenkin and Cox.[10] The value of k cited in the table was then calculated using $k_2/k = \{1.24-(280/T)\}$.

(e) Based on the same approach as for Comment (c), with E/R being taken from the data of Lightfoot *et al.*[1]

(f) k_{298} was based on the data of Cox and Tyndall,[11] Sander and Watson,[7] McAdam *et al.*,[12] Kurylo and Wallington,[8] Jenkin *et al.*,[13] Lightfoot *et al.*,[9] and Simon *et al.*[14] E/R was derived from the data of Sander and Watson,[7] Kurylo and Wallington,[8] Lightfoot *et al.*,[9] and Jenkin and Cox.[10]

Preferred Values

$k = 3.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.1 \times 10^{-13} \exp(365/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

$k_2 = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2 = 5.9 \times 10^{-13} \exp(-509/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–330 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.
$\Delta(E/R) = \pm 200$ K.
$\Delta \log k_2 = \pm 0.15$ at 298 K.
$\Delta(E_2/R) = \pm 300$ K.

Comments on Preferred Values

There have been no new data at or around room temperature and our previous recommendation,[2] which is in substantial agreement with other subsequent recommendations,[3-5] still stands. Here we repeat the comments of our last evaluation.

The most recent room temperature measurements[9,10,14] of k_{obs}/σ are in excellent agreement with our previously recommended value of $k_{obs}/\sigma(250 \text{ nm}) = 1.24 \times 10^5$ cm s^{-1}, which is unaltered. In addition, the measurements of the absorption cross-section by Simon *et al.*[14] are also in agreement with our previous recommendation of $\sigma(250 \text{ nm}) = 3.9 \times 10^{-18}$ cm^2 molecule^{-1} which is also unaltered. Thus, our earlier recommendation of $k_{obs} = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K[15] is confirmed.

Taking the revised branching ratio of $k_2/k = 0.30$ at 298 K (see below) yields the slightly revised value of k at 298 K listed above.

The temperature dependence of k reported by Lightfoot *et al.*[9] is in excellent agreement with the previous studies of Sander and Watson[7] and Kurylo and Wallington.[8] Here we have recommended the E/R value of Lightfoot *et al.*[9] on the basis of their more extensive temperature range. The recommended Arrhenius equation follows from the recommended values of k_{298} and E/R.

The two studies[9,16] of the temperature dependence of th branching ratio involve different temperature ranges. He we have selected the results of Horie *et al.*[16] over the mo atmospherically relevant temperature range of 200–330 K calculating the recommended value of k_2. This is deriv from the temperature-dependent value of k_2/k (see below and our recommended Arrhenius equation for k.

It should be noted that, from an analysis of their ow data[16] together with the results of Lightfoot *et al.*,[9] Anasta *et al.*,[6] Kan *et al.*,[17] Parkes,[18] Niki *et al.*,[19] and Weav *et al.*,[20] the equation $k_2/k = 1/\{1 + [\exp(1330/T)]/33\}$ was ob tained by Horie *et al.*[16] for the more extensive temperatu range 223–573 K. This equation shows slight non-Arrheni behavior.

Lightfoot *et al.*[9] observed no pressure dependence of th branching ratio, k_2/k, over the range 210–760 Torr.

References

[1] P. D. Lightfoot, P. Roussel, F. Caralp, and R. Lesclaux, J. Chem. So Faraday Trans. **87**, 3213 (1991).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (199
[4] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 180 (1992).
[5] NASA Evaluation No. 11, 1994 (see references in Introduction).
[6] C. Anastasi, I. W. M. Smith, and D. A. Parkes, J. Chem. Soc. Farada Trans. 1, **74**, 1693 (1978).
[7] S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980); **85**, 2960 (1981).
[8] M. J. Kurylo and T. J. Wallington, Chem. Phys. Lett. **138**, 543 (1987).
[9] P. D. Lightfoot, R. Lesclaux, and B. Veyret, J. Phys. Chem. **94**, 700 (1990).
[10] M. E. Jenkin and R. A. Cox, J. Phys. Chem. **95**, 3229 (1991).
[11] R. A. Cox and G. S. Tyndall, J. Chem. Soc. Faraday Trans. 2, **76**, 153 (1980).
[12] K. McAdam, B. Veyret, and R. Lesclaux, Chem. Phys. Lett. **133**, 39 (1987).
[13] M. E. Jenkin, R. A. Cox, G. D. Hayman, and L. J. Whyte, J. Chem. Soc. Faraday Trans. 2, **84**, 913 (1988).
[14] F. G. Simon, W. Schneider, and G. K. Moortgat, Int. J. Chem. **22**, 791 (1990).
[15] IUPAC, Supplement III, 1989 (see references in Introduction).
[16] O. Horie, J. N. Crowley, and G. K. Moortgat, J. Phys. Chem. **94**, 8198 (1990).
[17] C. S. Kan, J. G. Calvert, and J. H. Shaw, J. Phys. Chem. **84**, 3411 (1980).
[18] D. A. Parkes, Int. J. Chem. Kinet. **9**, 451 (1977).
[19] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **85**, 877 (1981).
[20] J. Weaver, J. Meagher, R. Shortridge, and J. Heicklen, J. Photochem. **4**, 341 (1975).

$CH_3O_2 + CH_3CO_3 \rightarrow CH_3O + CH_3CO_2 + O_2$ (1)
$\rightarrow CH_3CO_2H + HCHO + O_2$ (2)

$\Delta H^\circ(1) = -28$ kJ·mol^{-1}
$\Delta H^\circ(2) = -379$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Branching Ratios			
$k_2/k = 6.1\times10^{-6}\exp(2990/T)$	263–333	Horie and Moortgat, 1992[1]	(a)
Reviews and Evaluations			
$k_1 = 5.5\times10^{-12}$	298	IUPAC, 1992[2]	(b)
$k_2 = 5.5\times10^{-12}$	298		
$k_1 = 1.8\times10^{-9}\exp(-1800/T)$	298–368	Wallington, Dagaut, and Kurylo, 1992[3]	(b)
$k_2 = 4.1\times10^{-15}\exp(2100/T)$	298–368		
$5.1\times10^{-12}\exp(272/T)$	253–368	Lightfoot *et al.*, 1992[4]	(c)
$k_1/k_2 = 4.4\times10^5\exp(-3910/T)$	253–368		
1.1×10^{-11}	200–300	NASA, 1994[5]	(b)

Comments

(a) FTIR spectroscopic study of irradiated $CH_3COCOCH_3$ in the presence of Ar-O_2 mixtures at total pressures of 730–770 Torr. The reaction products CO_2, CO, HCHO, HCOOH, CH_3CO_2H, CH_3CO_3H, CH_3OH, H_2O_2, and O_3 were analyzed by matrix-isolation FTIR spectroscopy combined with a molecular-beam sampling technique. The branching ratio, $k_1/k_2 = 2.2\times10^6\exp(-3870/T)$, was derived from the yields of HCHO, CH_3CO_2H, HCO_2H, CH_3OH, and O_3.

(b) Based on the data of Moortgat *et al.*[6]

(c) Re-analysis of the data of Moortgat *et al.*[6]

Preferred Values

$k = 1.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.1\times10^{-12}\exp(272/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.

$k_2/k = 0.14$ at 298 K.

$k_2/k = 6.1\times10^{-6}\exp(2990/T)$ over the temperature range 260–350 K.

Reliability

$\Delta\log k = \pm0.3$ at 298 K.
$\Delta(E/R) = \pm300$ K.
$\Delta(k_2/k) = \pm0.1$ at 298 K.
$\Delta\ [(E_2-E)/R] = \pm500$ K.

Comments on Preferred Values

We have amended our previous recommendation of k slightly, to take account of the re-analysis by Lightfoot *et al.*[4] of the data of Moortgat *et al.*[6] The recent study of the products of this reaction by Horie and Moortgat,[1] leading to the temperature dependence of the branching ratio listed above, is much more direct than the earlier study of Moortgat *et al.*,[6] and is recommended.

References

[1] O. Horie and G. K. Moortgat, J. Chem. Soc. Faraday Trans. **88**, 3305 (1992).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).
[4] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).
[5] NASA Evaluation No. 11, 1994 (see references in Introduction).
[6] G. K. Moortgat, B. Veyret, and R. Lesclaux, J. Phys. Chem. **93**, 2362 (1989).

$$\begin{aligned} CH_3O_2 + CH_3COCH_2O_2 &\rightarrow CH_3OH + CH_3COCHO + O_2 \quad (1)\\ &\rightarrow HCHO + CH_3COCH_2OH + O_2 \quad (2)\\ &\rightarrow CH_3O + CH_3COCH_2O + O_2 \quad (3)\end{aligned}$$

Rate coefficient data ($k=k_1+k_2+k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comment
Absolute Rate Coefficients			
$(3.8\pm0.4)\times10^{-12}$	298	Bridier *et al.*, 1993[1]	(a)
Branching Ratios			
$k_1/k=(0.5\pm0.1)$	298	Jenkin *et al.*, 1992[2]	(b)
$k_2/k=(0.2\pm0.1)$	298		
$k_3/k=(0.3\pm0.1)$	298	Bridier *et al.*, 1993[1]	(c)

Comments

(a) Flash photolysis of Cl_2 in the presence of CH_3COCH_3-CH_4-N_2 mixtures at a total pressure of 760 Torr. The overall rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 230 and 260 nm.

(b) Steady-state photolysis of Cl_2 in the presence of CH_3COCH_3-N_2 mixtures at a total pressure of 700 Torr. Branching ratios were deduced from measurements of HCHO and CH_3COCHO products by long-path FTIR spectroscopy and long-path UV-VIS diode array spectroscopy.

(c) Derived from a kinetic analysis of the time-profiles obtained in the experiments described in Comment (a).

Preferred Values

$k=3.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k=0.5$ at 298 K.
$k_2/k=0.2$ at 298 K.
$k_3/k=0.3$ at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(k_1/k)=\Delta(k_2/k)=\Delta(k_3/k)=\pm0.15$ at 298 K.

Comments on Preferred Values

The preferred values of the rate coefficient and branching ratios are based on the measurements of Bridier *et al.*[1] and Jenkin *et al.*,[2] and require independent confirmation to reduce the assigned error limits.

References

[1] I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. **89**, 2993 (1993).
[2] M. E. Jenkin, R. A. Cox, M. Emrich, and G. K. Moortgat, J. Chem. Soc. Faraday Trans. **89**, 2983 (1993).

$$\begin{aligned} HOCH_2O_2 + HOCH_2O_2 &\rightarrow HCOOH + CH_2(OH)_2 + O_2 \quad (1)\\ &\rightarrow 2HOCH_2O + O_2 \quad (2)\end{aligned}$$

No new data have been published since our last evaluation.

Preferred Values

$k_1=7.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1=5.7\times10^{-14}\exp(750/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 275–325 K.
$k_2=5.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k_1=\pm0.3$ at 298 K.
$\Delta(E_1/R)=\pm750$ K.
$\Delta\log k_2=\pm0.3$ at 298 K.

Comments on Preferred Values

The parallel studies of Veyret *et al.*[1] and Burrows *et al.*[2] confirm that the interaction of $HOCHO_2$ radicals involves two channels. The two reports[1,2] of the rate coefficient k_1 at room temperature are in good agreement, and indicate that this channel is a factor of ~3–4 faster than the analogous interaction of CH_3O_2 radicals. The rate coefficient k_2 is even higher than k_1, with a value ~50 times that of the analogous reaction of CH_3O_2 radicals. The preferred values are identical to our previous evaluation, IUPAC, 1992.[3] Confirmation of the temperature coefficient of k_1 is needed, as well as a determination of the temperature coefficient of k_2.

References

[1] B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K. Moortgat, J. Phys. Chem. **93**, 2368 (1989).

[2] J. P. Burrows, G. K. Moortgat, G. S. Tyndall, R. A. Cox, M. E. Jenkin, G. D. Hayman, and B. Veyret, J. Phys. Chem. **93**, 2375 (1989).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\begin{aligned} C_2H_5O_2 + C_2H_5O_2 &\rightarrow C_2H_5OH + CH_3CHO + O_2 \quad &(1)\\ &\rightarrow 2C_2H_5O + O_2 &(2)\\ &\rightarrow C_2H_5OOC_2H_5 + O_2 &(3)\end{aligned}$$

$\Delta H^\circ(1) = -343.2$ kJ mol^{-1}
$\Delta H^\circ(2) = 23.0$ kJ mol^{-1}

Rate coefficient data ($k=k_1+k_2+k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
[illegible]$\times 10^{-14}$ exp[(60±40)/T]	248–460	Fenter *et al.*, 1993[1]	(a,b)
([illegible].9±0.5)$\times 10^{-14}$	298		
Reviews and Evaluations			
[illegible]$\times 10^{-14}$ exp(−110/T)	250–450	IUPAC, 1992[2]	(a,c)
[illegible]$\times 10^{-14}$ exp(−125/T)	260–380	Wallington, Dagaut, and Kurylo, 1992[3]	(a,d)
[illegible]$\times 10^{-14}$ exp(−100/T)	228–457	Lightfoot *et al.*, 1992[4]	(a,e)
[illegible]$\times 10^{-14}$	200–300	NASA, 1994[5]	(a,f)

Comments

(a) k is defined by $-d[C_2H_5O_2]/dt = 2k[C_2H_5O_2]^2$ and is derived from the observed overall second-order decay of $C_2H_5O_2$ radicals.

(b) Flash photolysis-UV absorption study of Cl_2-C_2H_6-O_2-N_2 mixtures at 760 Torr total pressure. Rate coefficients were derived from simultaneous computer analyses of several decay curves collected at different wavelengths. The value of $k_{obs}=(1.40\pm0.11)\times10^{-13}\times\exp[(-20\pm40)/T]$ cm^3 molecule^{-1} s^{-1} was corrected[4] at each temperature by dividing by $(1+\alpha)$, where $\alpha=\beta/(1+\beta)$ and $\beta=10.2\exp(-533/T)$.

(c) k_{298} was calculated from the mean k_{obs} value from the studies of Adachi *et al.*,[6] Anastasi *et al.*,[7] Cattell *et al.*,[8] Wallington *et al.*,[9] and Bauer *et al.*,[10] and corrected for secondary removal of $C_2H_5O_2$ radicals by the use of $k_2/k=0.62$. E/R was from the study of Wallington *et al.*[9]

(d) k_{298} was calculated from $k_{obs}=2.1\times10^{-13}\times\exp(-250/T)$ cm^3 molecule^{-1} s^{-1}, derived from least-squares analysis of the data of Anastasi *et al.*[11] and Wallington *et al.*[9] and corrected for secondary removal of $C_2H_5O_2$ radicals by the use of $k_2/k=\{1.33-(209/T)\}$.

(e) k_{298} was calculated from the mean value of k_{obs} from the data of Adachi *et al.*,[6] Anastasi *et al.*,[7] Cattell *et al.*,[8] Wallington *et al.*,[9] and Bauer *et al.*,[10] and was corrected for secondary removal of $C_2H_5O_2$ radicals by the use of $k_2/k=0.63$. E/R was the average from the data of Anastasi *et al.*,[7] Cattell *et al.*,[8] Wallington *et al.*,[9] and Bauer *et al.*[10]

(f) k_{298} was calculated from the mean k_{obs} value from the studies of Cattell *et al.*,[8] Wallington *et al.*,[9] Bauer *et al.*,[10] and Fenter *et al.*,[1] and corrected for secondary removal of $C_2H_5O_2$ radicals by the use of $k_2/k = 0.6$. E/R was from the studies of Anastasi *et al.*,[7,11] Cattell *et al.*,[8] Wallington *et al.*,[9] Bauer *et al.*,[10] and Fenter *et al.*[1]

Preferred Values

$k=6.4\times10^{-14}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–450 K.
$k_2/k=0.62$ at 298 K.

Reliability
$\Delta\log k=\pm0.12$ at 298 K.
$\Delta(E/R)=^{+300}_{-100}$ K.
$\Delta(k_2/k)=\pm0.1$ at 298 K.

Comments on Preferred Values

The rate coefficients reported by Fenter *et al.*[1] are in good agreement with previous data for this reaction.[2] The temperature coefficient reported in the same study[1] ($E/R=-60$ K) agrees with the data of Cattell *et al.*[8] ($E/R\simeq0$ K) but less well with those of Anastasi *et al.*[7] ($E/R=470$ K), Wallington *et al.*[9] ($E/R=110$ K), or Bauer *et al.*[10] ($E/R=-230$ K). In view of the small temperature coefficients reported in most of these studies, together with the relatively large associated error limits, we have selected a temperature-independent rate coefficient k based on k_{298}. Thus, from the data of Adachi *et al.*,[6] Anastasi *et al.*,[7] Cattell *et al.*,[8] Wallington *et al.*,[9] and Fenter *et al.*,[1] the average value of $k_{obs}=1.03\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K. Taking $k_2/k=0.62$ at 298 K (the mean of the data of Niki *et al.*,[12] Anastasi *et al.*,[7] and Wallington *et al.*[13]) yields the recommended value of $k_{298}=6.4\times10^{-14}$ cm^3 molecule^{-1} s^{-1}.

The temperature dependence of the branching ratio reported by Anastasi *et al.*[7] still requires confirmation.

References

[1] F. F. Fenter, V. Catoire, R. Lesclaux, and P. D. Lightfoot, J. Phys. Chem. **97**, 3530 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).

[4] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayma E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**. (1992).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

[6] H. Adachi, N. Basco, and D. G. L. James, *Int. J. Chem. Kinet.* **11**. (1979).

[7] C. Anastasi, D. J. Waddington, and A. Woolley, J. Chem. Soc. Fa Trans. 1, **79**, 505 (1983).

[8] F. C. Cattell, J. Cavanagh, R. A. Cox, and M. E. Jenkin, J. Chem. Faraday Trans. 2, **82**, 1999 (1986).

[9] T. J. Wallington, P. Dagaut, and M. J. Kurylo, J. Photochem. **42**. (1988).

[10] D. Bauer, J. N. Crowley, and G. K. Moortgat, J. Photochem. Photo **A65**, 329 (1992).

[11] C. Anastasi, M. J. Brown, D. B. Smith, and D. J. Waddington, J Meeting of the French and Italian Sections of the Combustion Insti Amalfi, June 1987.

[12] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Ph Chem. *86*, *3825* (*1982*).

[13] T. J. Wallington, C. A. Gierczak, J. C. Ball, and S. M. Japar, Int. J. Ch Kinet. **21**, 1077 (1989).

$$CH_3OCH_2O_2 + CH_3OCH_2O_2 \rightarrow CH_3OCH_2OH + CH_3OCHO + O_2 \quad (1)$$

$$\rightarrow 2CH_3OCH_2O + O_2 \quad (2)$$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comme
Absolute Rate Coefficients			
$(2.7\pm0.4)\times10^{-12}$	300	Dagaut, Wallington, and Kurylo, 1989[1]	(a,b)
$(2.1\pm0.3)\times10^{-12}$	298	Jenkin *et al.*, 1993[2]	(c)
Branching Ratios			
$k_2/k=(0.67\pm0.11)$	295	Jenkin *et al.*, 1993[2]	(d)
$k_2/k=(0.67\pm0.13)$	298	Jenkin *et al.*, 1993[2]	(e)
Reviews and Evaluations			
2.7×10^{-12}	298	Lightfoot *et al.*, 1992[3]	(f)

Comments

(a) k is defined by $-d[CH_3OCH_2O_2]/dt = 2k[CH_3OCH_2O_2]^2$ and has been derived from the measured overall second-order decay of $CH_3OCH_2O_2$ radicals (k_{obs}).

(b) Flash photolysis of Cl_2-CH_3OCH_3-O_2-N_2 mixtures at total pressures of 25–800 Torr from 228 to 380 K. $CH_3OCH_2O_2$ radicals were monitored by UV absorption with $\sigma_{240}=(3.65\pm0.35)\times10^{-18}$ cm^2 molecule^{-1}. k_{obs} showed a strong pressure dependence and when treated by the Troe theory as a simple association reaction in the fall-off region, with a fixed $F_c=0.6$, the following expressions were derived for the low and high-pressure limiting rate coefficients: $k_0=(2.5\pm0.4)\times10^{-30}$ $(T/300\text{ K})^{-(5.0\pm0.5)}$ cm^6 molecule^{-2} s^{-1} and $k_\infty=(2.7\pm0.2)\times10^{-12}$ $(T/300)^{-(4.5\pm0.4)}$ cm^3 molecule^{-1} s^{-1}.

(c) Molecular modulation study of Cl_2-CH_3OCH_3-O_2-N_2 mixtures together with a pulse radiolysis study of SF_6-CH_3OCH_3-O_2 mixtures. k_{obs} was found to be dependent on the total pressure (17–760 Torr) and on the composition of the reaction mixture. On the basis of a mechanism involving the generation of H atoms via the reaction $CH_3OCH_2O + M \rightarrow CH_3OCHO + H + M$, it was possible to derive the above pressure-independent value of k.

(d) FTIR spectroscopic study of the steady-state photolysis of Cl_2 in the presence of CH_3OCH_3-O_2-N_2 mixtures over the total pressure range 10–700 Torr. The branching ratio was determined from the yields of CH_3OCHO and CH_3OCH_2OOH. Minor amounts of CH_3OCH_2OH were also observed.

(e) Similar study to that described in Comment (c). The branching ratio and k were derived from a kinetic analysis of the effects of $[O_2]$ and $[Cl_2]$ on k_{obs}, based on a mechanism including the production of H atoms from the reaction $CH_3OCH_2O + M \rightarrow CH_3OCHO + H + M$.

Based on the data of Dagaut *et al.*[1]

Preferred Values

$k = 2.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.67$ at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The apparent effect of total pressure on k, the first reported for this type of reaction,[1] has been shown to be an artifact by the more recent experiments of Jenkin *et al.*[2] This comprehensive study[2] has shown that the pressure effect was due to secondary chemistry involving H atoms which arise from the reaction $CH_3OCH_2O + M \rightarrow CH_3OCHO + H + M$. A kinetic analysis of the molecular modulation system, allowing for secondary chemistry, yielded the preferred rate coefficient. At the same time the derived value of the branching ratio,[2] k_2/k, is in excellent agreement with that obtained from a steady-state photolysis system with FTIR spectroscopic analyses.[2]

References

[1] P. Dagaut, T. J. Wallington, and M. J. Kurylo, J. Photochem. Photobiol. **48**, 187 (1989).
[2] M. E. Jenkin, G. D. Hayman, T. J. Wallington, M. D. Hurley, J. C. Ball, O. J. Nielsen, and T. Ellermann, J. Phys. Chem. **97**, 11712 (1993).
[3] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).

$CH_3CO_3 + CH_3CO_3 \rightarrow 2CH_3CO_2 + O_2$

$\Delta H° = -71$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.8 \times 10^{-12} \exp(530/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.

Reliability
$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The agreement among the three measurements[1–3] of this rate coefficient at room temperature is rather poor. The most recent study of Moortgat *et al.*[3] is selected as the basis for our recommendation, on the grounds that it is based upon a more complete knowledge of the complicated chemistry involved than was available for the earlier studies.[1,2] At the same time, until more experimental data are available we have assigned considerable error limits, particularly with regard to the temperature coefficient. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] M. C. Addison, J. P. Burrows, R. A. Cox, and R. Patrick, Chem. Phys. Lett. **73**, 283 (1980).
[2] N. Basco and S. S. Parmar, Int. J. Chem. Kinet. **17**, 891 (1985).
[3] G. K. Moortgat, B. Veyret, and R. Lesclaux, J. Phys. Chem. **93**, 2362 (1989).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$$CH_3CO_3 + CH_3COCH_2O_2 \rightarrow CH_3COOH + CH_3COCHO + O_2 \quad (1)$$
$$\rightarrow CH_3 + CO_2 + CH_3COCH_2O + O_2 \quad (2)$$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Commen
Absolute Rate Coefficients			
$(5.0\pm2.0)\times10^{-12}$	298	Bridier *et al.*, 1993[1]	(a)
$k_1\leq4\times10^{-12}$	298		
Branching Ratios			
$k_2/k=(0.5\pm0.2)$	298	Jenkin *et al.*, 1993[2]	(b)

Comments

(a) Flash photolysis of Cl_2 in the presence of CH_3COCH_3-CH_3CHO-N_2 mixtures at a total pressure of 760 Torr. The rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 210, 220, 230, and 245 nm, using the value of $k_2/k=0.5$ determined by Jenkin *et al.*[2]

(b) Steady-state photolysis of Cl_2 in the presence of CH_3COCH_3-N_2 mixtures at a total pressure of 700 Torr. The branching ratio was deduced from measurements of HCHO and CH_3COCHO products by long-path FTIR spectroscopy and long-path UV-VIS diode array spectroscopy.

Preferred Values

$k=5.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1\leq4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k=0.5$ at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(k_2/k)=\pm0.2$ at 298 K.

Comments on Preferred Values

The preferred values of the rate coefficient and the branching ratio are from the studies of Bridier *et al.*[1] and Jenki *et al.*,[2] and require independent confirmation.

References

[1] I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, J. Chem. Soc. Far day Trans. **89**, 2993 (1993).
[2] M. E. Jenkin, R. A. Cox, M. Emrich, and G. K. Moortgat, J. Chem. So Faraday Trans. **89**, 2983 (1993).

$$HOCH_2CH_2O_2 + HOCH_2CH_2O_2 \rightarrow HOCH_2CH_2OH + HOCH_2CHO + O_2 \quad (1)$$
$$\rightarrow 2HOCH_2CH_2O + O_2 \quad (2)$$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Commen
Branching Ratios			
$k_2/k=0.5\pm0.1$	298	Barnes, Becker, and Ruppert, 1993[1]	(a)
Reviews and Evaluations			
2.3×10^{-12}	298	IUPAC, 1992[2]	(b,c)
$k_2/k=0.36$	298		

Comments

(a) Steady-state photolysis at 254 nm of $HOCH_2CH_2I$-N_2-O_2 or H_2O_2-C_2H_4-N_2-O_2 mixtures at pressures of 150–900 mbar with FTIR spectroscopic detection of the products HCHO, $HOCH_2CHO$, and $HOCH_2CH_2OH$. Values of $k_2/k=0.49\pm0.05$ and 0.5 ±0.04 were derived from the two different reacta systems, independent of total pressure O_2 partial pressure.

(b) k is defined by $-d[HOCH_2CH_2O_2]/d$ $=2k[HOCH_2CH_2O_2]^2$ and has been derived from the measured overall second-order decay of $HOCH_2CH_2O_2$ radicals (k_{obs}) by correcting for secondary removal of $HOCH_2CH_2O_2$.

k_{298} was based on the data of Jenkin and Cox,[3] Anastasi *et al.*,[4] and Murrells *et al.*,[5] and k_2/k was from the data of Murrells *et al.*[5]

Preferred Values

$k = 2.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2/k = 0.5$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value of k_{298} is identical to our previous evaluation, IUPAC, 1992.[2] The recent measurements of the branching ratio, k_2/k, by Barnes *et al.*[1] are based on direct measurements of the products of the reaction channels and are also independent of the source of the radicals. For these reasons their branching ratio[1] is preferred to the earlier, less direct determination of Murrells *et al.*[5]

References

[1] I. Barnes, K. H. Becker, and L. Ruppert, Chem. Phys. Lett. **203**, 295 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] M. E. Jenkin and R. A. Cox, J. Phys. Chem. **95**, 3229 (1991).

[4] C. Anastasi, D. J. Muir, V. J. Simpson, and P. Pagsberg, J. Phys. Chem. **95**, 5791 (1991).

[5] T. P. Murrells, M. E. Jenkin, S. J. Shalliker, and G. D. Hayman, J. Chem. Soc. Faraday Trans. **87**, 2351 (1991).

$n\text{-}C_3H_7O_2 + n\text{-}C_3H_7O_2 \rightarrow n\text{-}C_3H_7OH + C_2H_5CHO + O_2 \quad (1)$

$\rightarrow 2n\text{-}C_3H_7O + O_2 \quad (2)$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The recommended rate coefficient is the rounded-off value from the study of Adachi and Basco,[1] and is identical to our previous evaluation, IUPAC, 1992.[2] The room temperature rate coefficient requires substantiation along with a determination of the temperature coefficient.

The recommended value of k_{298} is in line with the rate coefficients of the analogous reactions of the CH_3O_2 and $C_2H_5O_2$ radicals. On the other hand, the recommended rate coefficient for the self-reaction of the $i\text{-}C_3H_7O_2$ radical is considerably lower ($k_{298} = 1.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}) and that reported[3] for the $t\text{-}C_4H_9O_2$ radical is even lower still ($k_{298} = 2.3 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}). This trend is in keeping with that observed in the liquid phase for the RO_2 radical interactions,[4] i.e., $k(\text{primary } RO_2) > k(\text{secondary } RO_2) > k(\text{tertiary } RO_2)$.

References

[1] H. Adachi and N. Basco, Int. J. Chem. Kinet. **14**, 1125 (1982).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] C. Anastasi, I. W. M. Smith, and D. A. Parks, J. Chem. Soc. Faraday Trans. 1, **74**, 1693 (1978).

[4] J. E. Bennett, D. M. Brown, and B. Mile, Trans. Faraday Soc. **66**, 386 (1970).

$i\text{-}C_3H_7O_2 + i\text{-}C_3H_7O_2 \rightarrow i\text{-}C_3H_7OH + (CH_3)_2CO + O_2 \quad (1)$

$\rightarrow 2i\text{-}C_3H_7O + O_2 \quad (2)$

$\Delta H^\circ(1) = -351.9$ kJ·mol^{-1}

$\Delta H^\circ(2) = -33.2$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 1.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.6\times10^{-12}\exp(-2200/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–400 K.
$k_1/k = 0.44$ at 298 K.
$k_1/k = 3.7\times10^{-2}\exp(740/T)$ over the temperature range 300–400 K.
$k_2/k = 0.56$ at 298 K.
$k_2/k = 2.0\exp(-380/T)$ over the temperature range 300–400 K.

Reliability
$\Delta\log k = \pm0.3$ at 298 K.
$\Delta(E/R) = \pm300$ K.
$\Delta(k_1/k) = \Delta(k_2/k) = \pm0.15$ at 298 K.

Comments on Preferred Values

The recommended rate coefficient (k) at 298 K is the average of the rate coefficients from the data of Kirsch *et al.*[1,2] and Adachi and Basco,[3] which are in reasonable agreement. We have not taken into account the rate coefficient reported by Munk *et al.*,[4] for which experimental details are lacking. The recommended temperature dependence of k is based on the results of Kirsch *et al.*,[1] which have been rounded to and adjusted to the recommended value of k_{298}.

The measurements of the branching ratio and its temperature dependence[2,5] appear to be reliable and have been adopted here, but require further confirmation. The preferred values are identical to our previous evaluation, IUPAC 1992.[6]

The value of k_{298} is considerably lower than that for the analogous reaction of the n-$C_3H_7O_2$ radical, which is in keeping with the trend observed in studies of the interaction of alkylperoxy radicals in solution,[7] i.e., k(primary RO_2) $>k$(secondary RO_2) $>k$(tertiary RO_2).

References

[1] L. J. Kirsch, D. A. Parkes, D. J. Waddington, and A. Woolley, J. Chem. Soc. Faraday. Trans. 1, **74**, 2293 (1978).
[2] L. J. Kirsch, D. A. Parkes, D. J. Waddington, and A. Woolley, J. Chem. Soc. Faraday Trans. 1, **75**, 2678 (1979).
[3] H. Adachi and N. Basco, Int. J. Chem. Kinet. **14**, 1125 (1982).
[4] J. Munk, P. Pagsberg, E. Ratajczak, and A. Sillesen, Chem. Phys. Lett. **132**, 417 (1986).
[5] L. T. Cowley, D. J. Waddington, and A. Woolley, J. Chem. Soc. Faraday Trans. 1, **78**, 2535 (1982).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).
[7] J. E. Bennett, D. M. Brown, and B. Mile, Trans Faraday Soc. **66**, 386 (1970).

$$\mathrm{CH_3COCH_2O_2 + CH_3COCH_2O_2 \rightarrow CH_3COCH_2OH + CH_3COCHO + O_2} \quad (1)$$
$$\mathrm{\rightarrow 2CH_3COCH_2O + O_2} \quad (2)$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.0\pm0.2)\times10^{-12}$	298	Bridier *et al.*, 1993[1]	(a,b)
Branching Ratios			
$k_2/k = (0.75\pm0.1)$	298	Bridier *et al.*, 1993[1]	(c)
Reviews and Evaluations			
$\leq1\times10^{-11}$	298	IUPAC, 1992[2]	(d)
8.3×10^{-12}	298	Wallington, Dagaut, and Kurylo, 1992[3]	(d)
8.3×10^{-12}	298	Lightfoot *et al.*, 1992[4]	(d)

Comments

(a) k is defined by $-d[CH_3COCH_2O_2]/dt = 2k[CH_3COCH_2O_2]^2$.

(b) Flash photolysis of Cl_2 in the presence of CH_3COCH_3-N_2 mixtures at a total pressure of 760 Torr. The rate coefficient k was derived from a kinetic analysis of absorption-time profiles at 230 and 260 nm, taking account of the information on the mechanism of the overall reaction obtained from the product study of Jenkin *et al.*[5]

(c) Same experiments as for Comment (a). The branching ratio was obtained on the basis of absorption due to radicals formed in reaction (2) and subsequent reactions.

(d) Based on the data of Cox *et al.*[6]

Preferred Values

$k = 8.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.75$ at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The above recommendations on the overall rate coefficient and the branching ratio at 298 K require independent verification.

References

[1] I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. **89**, 2993 (1993).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).
[4] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).
[5] M. E. Jenkin, R. A. Cox, M. Emrich, and G. K. Moortgat, J. Chem. Soc. Faraday Trans. **89**, 2983 (1993).
[6] R. A. Cox, J. Munk, O. J. Nielsen, P. Pagsberg, and E. Ratajczak, Chem. Phys. Lett. **173**, 206 (1990).

$$\mathrm{RCHOO + O_3 \longrightarrow RCHO + 2\,O_2} \qquad (1)$$

$$\mathrm{RCHOO + H_2O \longrightarrow products} \qquad (2)$$

$$\mathrm{RCHOO + CO \longrightarrow products} \qquad (3)$$

$$\mathrm{RCHOO + HCHO \longrightarrow R\overline{CHOOCH_2O}} \qquad (4)$$

$$\mathrm{RCHOO + C_2H_4 \longrightarrow products} \qquad (5)$$

$$\mathrm{RCHOO + NO \longrightarrow RCHO + NO_2} \qquad (6)$$

$$\mathrm{RCHOO + NO_2 \longrightarrow RCHO + NO_3} \qquad (7)$$

$$\mathrm{RCHOO + SO_2 \longrightarrow products} \qquad (8)$$

(R=H or CH_3)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Biradical	Temp./K	Reference	Comm
Relative Rate Coefficients				
$k_2/k_8=(6.1\pm0.3)\times10^{-5}$	CH_3CHOO	295	Calvert *et al.*, 1978[1]	(a)
$k_1:k_3:k_4:k_5:k_8=2.5\times10^{-3}:1.8\times10^{-3}:2.5\times10^{-1}:2.5\times10^{-3}:1.0$	CH_2OO	296	Su, Calvert, and Shaw, 1980[2]	(b)
$k_2/k_8=(2.3\pm1)\times10^{-4}$	CH_2OO	298	Suto, Manzanares, and Lee, 1984[3]	(c)
$k_7/k_8=(1.4\pm0.4)\times10^{-2}$	CH_2OO	298	Manzanares, Suto, and Lee, 1987[4]	(d)
$k_2/k_8=(8.3\pm3.6)\times10^{-4}$	CH_2OO	298	Becker, Bechara, and Brockman, 1993[5]	(e)
$k_2/k_8=(4.1\pm2.2)\times10^{-4}$	$(CH_3)_2COO$	298	Becker, Bechara, and Brockman, 1993[5]	(f)
Reviews and Evaluations				
$k_2=2\times10^{-19}$ to 1×10^{-15}	CH_2OO	298	Herron, Martinez, and Huie, 1982[6]	(g)
$k_4-2\times10^{-16}$ to 8×10^{-13}	CH_2OO	298		(h)
$k_7=1\times10^{-17}$ to 7×10^{-14}	CH_2OO/ CH_3CHOO	298		(i)
$k_8=3\times10^{-15}$ to 1.7×10^{-11}	CH_2OO/ CH_3CHOO	298		(j)
$k_2:k_3:k_4:k_6:k_7:k_8=5\times10^{-5}:2\times10^{-3}:0.25:10^2:10:1$	CH_2OO/ CH_3CHOO	298	Atkinson, and Lloyd, 1984[7]	(k)
$k_2\sim4\times10^{-18}$	CH_2OO/ CH_3CHOO	298		(l)
$k_4\sim2\times10^{-14}$	CH_2OO/ CH_3CHOO	298		(l)
$k_6=7\times10^{-12}$	CH_2OO/ CH_3CHOO	298		(m)
$k_7\sim7\times10^{-13}$	CH_2OO/ CH_3CHOO	298		(l)
$k_8\sim7\times10^{-14}$	CH_2OO/ CH_3CHOO	298		(l)
$k_2=4\times10^{-16}$	CH_2OO	298	Kerr and Calvert, 1984[8]	(n)
$k_3=1.3\times10^{-14}$	CH_2OO	298		(n)
$k_4=2\times10^{-12}$	CH_2OO	298		(n)
$k_6=7\times10^{-12}$	CH_2OO/ CH_3CHOO	298		(n)
$k_7=1.0\times10^{-13}$	CH_2OO/ CH_3CHOO	298		(n)
$k_8=7\times10^{-12}$	CH_2OO	298		(n)

Comments

(a) Derived from a reanalysis of the data of Cox and Penkett[9] from a study of the aerosol formation from SO_2 in the presence of O_3-O_2-*cis*-2-C_4H_8 mixtures at atmospheric pressure. In this system the biradical intermediate involved is believed to be $CH_3\dot{C}HO\dot{O}$.

(b) FTIR study of the C_2H_4-O_3 reaction in the presence of O_2-N_2 mixtures at a total pressure of 700 Torr and with added CO, HCHO, or SO_2. Relative rate coefficients derived from a computer simulation of reactant consumption and product formation, based on a mechanism of 20 elementary reactions.

(c) Flow system involving C_2H_4-O_3-SO_2-H_2O mixtures in which H_2SO_4 aerosol concentrations were monitored by scattered UV light. Relative rate coefficients obtained from the dependencies of the aerosol formation on the concentrations of O_3, SO_2, and H_2O.

(d) Similar study to that of comment (c), with the inclusion of the effect of added NO_2 on the formation of the H_2SO_4 aerosol.

(e) Study of the C_2H_4-O_3 reaction in the presence of 1 atm of synthetic air with and without added SO_2; H_2O_2 yields were measured by tunable diode laser absorption spectroscopy or by FTIR spectroscopy.

(f) Same study as for comment (e) with $(CH_3)_2C{=}C(CH_3)_2$ as the reactant.

(g) Based on the ratio $k_2/k_8 \approx 6\times10^{-5}$, as derived by Calvert *et al.*[1] from the data of Cox and Penkett,[9] and taking $3\times10^{-15} < k_8 < 1.7\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [see comment (k)].

(h) Based on a study of the ozonide formation in the system O_3-O_2-*cis*-2-C_4H_8-HCHO by Niki *et al.*[10] and on thermochemical kinetic estimates of Nangia and Benson.[11] Details were not provided. It has been assumed that the reactivities of the $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$ biradicals are identical.

(i) Derived from the ratio $k_4/k_7 \approx 14$, which has been estimated from the data of Martinez *et al.*[12] from a study of the reduction in secondary ozonide formation from the O_3-O_2-*trans*-2-C_4H_8 reaction in the presence of NO_2. k_7 was calculated by taking $2\times10^{-16} < k_4 < 8\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} [see comment (h)]. It has been assumed that the reactivities of the $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$ biradicals are identical.

(j) Based on the suppression of ozonide formation in the O_3-O_2-*cis*-2-C_4H_8-HCHO system by SO_2 observed by Niki *et al.*[10] and on thermochemical kinetic estimates of Nangia and Benson.[11] Details were not provided. It has been assumed that the reactivities of the $\dot{C}H_2O\dot{O}$ and $CH_2\dot{C}HO\dot{O}$ biradicals are identical.

(k) The relative rate coefficients are proposed on the basis that the data on $\dot{C}H_2O\dot{O}$ (Su *et al.*[2]) and on $CH_3\dot{C}HO\dot{O}$ (Cox and Penkett[9]) can be amalgamated, i.e., $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$ have the same reactivities. From the studies of Akimoto *et al.*[13,14] on the O_3-C_2H_4 and C_3H_6 system, it was estimated that $k_6{:}k_7{:}k_8 = 10^2{:}10{:}1$.

(l) Calculated from the above relative rate coefficients and assuming that $k_6 = 7\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} [see comment (m)].

(m) This rate coefficient was assumed to have a value similar to that for the reaction of alkylperoxy radicals with NO ($RO_2 + NO \rightarrow RO + NO_2$), and hence $k_6 = 7\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

(n) Calculated (i) on the assumption that $k_6 = k_8$ and taking the estimated value of $k_6 = 7\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} of Atkinson and Lloyd[7] and (ii) from the relative rate data of Calvert *et al.*,[1] Su *et al.*,[2] and Suto *et al.*[3]

Preferred Values

No recommendation.

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation, IUPAC, 1992.[15] Vibrationally excited Criegie intermediates or biradicals, $[R\dot{C}HO\dot{O}]^\ddagger$, are produced from the reactions of O_3 with alkenes.[16] These species decompose unimolecularly to give molecular or radical products or undergo collisional deactivation to yield thermally equilibrated biradicals, $R\dot{C}HO\dot{O}$. Here we consider the kinetic and other information relating to the bimolecular reactions that have been proposed for these thermally equilibrated biradicals

Studies have been made of the reactions of $R\dot{C}HO\dot{O}$ with aldehydes,[2,10,17–20] SO_2[1,2,9,10,21] and H_2O,[1,9,13,22] but detailed kinetic data are often lacking. Relative rate coefficients have been derived by Calvert *et al.*,[1] Su *et al.*,[2] and Suto *et al.*[3] based on experimental measurements of the rates of consumption of molecular reactants relative to consumption of SO_2 in systems involving $R\dot{C}HO\dot{O}$ biradicals. The only compound, other than SO_2, common to any of these studies is H_2O, for which the derived relative rate coefficients differ by a factor of ~4. Notwithstanding this discrepancy, these relative rate measurements are the only experimental basis on which to assess the rates of these reactions. It is apparent from these measurements that the reactions of the biradicals $CH_3\dot{C}HO\dot{O}$ with O_3, CO and alkenes are not important under atmospheric conditions. The reactions with H_2O, RCHO, NO_2, and SO_2 need to be considered, although for most tropospheric conditions the only effective reaction of the biradicals is likely to be that with H_2O.

Previous reviewers[7,8] have made the reasonable assumption that the reaction of $R\dot{C}HO\dot{O}$ with NO could also be significant, based on estimates of the energetics of the proposed reaction pathway $R\dot{C}HO\dot{O} + NO \rightarrow RCHO + NO_2$. Unfortunately, there is no direct experimental evidence for this reaction and very little information upon which to base an estimate of its rate coefficient. Atkinson and Lloyd[7] have estimated the relative rate coefficients for $R\dot{C}HO\dot{O}$ reacting with NO and SO_3, corresponding to $k_6/k_7 = 10^2$, whereas Kerr and Calvert[8] propose $k_6/k_7 = 1$. Experimental data on this ratio of rate coefficients are badly needed.

In the absence of direct kinetic measurements of the absolute rate coefficients of any of the $R\dot{C}HO\dot{O}$ bimolecular reactions, both Atkinson and Lloyd[7] and Kerr and Calvert[8] have suggested that k_6 should be equated to the rate coefficient for the structurally analogous reactions, $RO_2 + NO \rightarrow RO + NO_2$, with $k_6 = 7\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. While this seems a reasonable proposition, it is desirable to obtain experimental verification. At present it is difficult to see how any direct measurements could be made with $R\dot{C}HO\dot{O}$ systems involving O_3-alkene reactions owing to the complex chemistry involved. In this regard the recent studies of Hatakeyama *et al.*[22] involving the generation of $\dot{C}H_2O\dot{O}$ biradicals from the reaction of $CH_2(^3B_1)$ with O_2 are of considerable interest.

In deriving the relative rate coefficients listed above, it has been necessary to compare data obtained from different O_2-alkene systems and to assume that all the $R\dot{C}HO\dot{O}$ biradicals have equal reactivity, e.g., $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$. Again, while this seems to be a reasonable assumption, it requires experimental verification.

There is very little direct experimental evidence on the products of any of the reactions (1) to (8). Where the products are stated these have largely been suggested on the basis of analogy with related reactions.

In addition to the expected formation of carboxylic acids from the reactions of the biradicals with H_2O,

$$R\dot{C}HO\dot{O} + H_2O \rightarrow RCOOH + H_2O,$$

recent studies of the reactions of O_3 with *trans*-2-butene,[5,23,24] isoprene,[23,24] and monoterpenes[23,24] have reported varying amounts of H_2O_2 product. Since the yields of H_2O_2 were considerably enhanced by the presence of H_2O, it was proposed that H_2O_2 was formed in a direct reaction involving Criegie biradicals:

$$R_1R_2\dot{C}O\dot{O} + H_2O \rightarrow (R_1R_2COO{\cdot}H_2O)$$

$$(R_1R_2COO{\cdot}H_2O) \rightarrow R_1COR_2 + H_2O_2$$

In some of these experiments,[23] as in previous O_3-alkene studies,[25,26] hydroperoxides were also detected as products. The hydroperoxides were suggested to arise also from a direct Criegie biradical-H_2O interaction:

$$R_1R_2\dot{C}O\dot{O} + H_2O \rightarrow R_1R_2C(OH)OOH.$$

References

[1] J. G. Calvert, F. Su, J. W. Bottenheim, and O. P. Strausz, Atmos. Environ. **12**, 197 (1978).

[2] F. Su, J. G. Calvert, and J. H. Shaw, J. Phys. Chem. **84**, 239 (1980).

[3] M. Suto, E. R. Manzanares, and L. C. Lee, Environ. Sci. Technol. **19**, 81 (1985).

[4] E. R. Manzanares, M. Suto, and L. C. Lee (unpublished data).

[5] K. H. Becker, J. Bechara, and K. J. Brockman, Atmos. Environ. **27A**, (1993).

[6] J. T. Herron, R. I. Martinez, and R. E. Huie, Int. J. Chem. Kinet. **14**, 20 (1982).

[7] R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984

[8] J. A. Kerr and J. G. Calvert, *Chemical Transformation Modules for Eulerian Acid Deposition Models*, The Gas-Phase Chemistry Vol. 1 (National Center for Atmospheric Research, Boulder, CO, 1984).

[9] R. A. Cox and S. A. Penkett, J. Chem. Soc. Faraday Trans. 1, **68** 17 (1972).

[10] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Chem. Phys. Lett. **46**, 327 (1977).

[11] P. S. Nangia and S. W. Benson, Int. J. Chem. Kinet. **12**, 43 (1980).

[12] R. I. Martinez, R. E. Huie, and J. T. Herron, Chem Phys. Lett. **72**, 44 (1980).

[13] H. Akimoto, H. Bandow, F. Sakamaki, G. Inoue, M. Hoshino, and M Okuda, Research Report No. 9, R-9-79, National Institute for Environmental Studies, Japan, 1979.

[14] H. Akimoto. H. Bandow, F. Sakamaki, G. Inoue, M. Hoshino, and M Okuda, Environ. Sci. Technol. **14**, 172 (1980).

[15] IUPAC, Supplement IV, 1992 (see references in Introduction).

[16] R. Atkinson and W. P. L. Carter, Chem. Rev. **84**, 437 (1984).

[17] P. L. Hanst, E. R. Stephens, W. E. Scott, and R. C. Doerr, *Atmospheric Ozone-Olefin Reactions* (Franklin Institute, Philadelphia, PA, 1958).

[18] C. S. Kan, F. Su, J. G. Calvert, and J. H. Shaw, J. Phys. Chem. **85**, 235 (1981).

[19] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, presented at the International Conference on Environmental Sensing and Assessment, Las Vegas, NV, Vol. **2**, pp. 2-44 (1975).

[20] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **85**, 1024 (1981).

[21] S. Hatakeyama, H. Kobayashi, Z.-Y. Lin, H. Takagi, and H. Akimoto, J. Phys. Chem. **90**, 4131 (1986).

[22] S. Hatakeyama, H. Bandow, M. Okuda, and H. Akimoto, J. Phys. Chem. **85**, 2249 (1981).

[23] R. Simonaitis, K. J. Olszyna, and J. F. Meagher, Geophys. Res. Lett. **18**, (1990).

[24] K. H. Becker, K. J. Brockmann, and J. Bechara, Nature **346**, 256 (1990).

[25] R. I. Martinez, J. T. Herron, and R. E. Huie, J. Am. Chem. Soc. **103**, 3807 (1981).

[26] S. Gäb, E. Hellpointer, W. V. Turner, and F. Kórte, Nature **316**, 535 (1985).

$O_3 + C_2H_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k = 1 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 1.0$ at 298 K.

Comments on Preferred Values

The literature data[1–6] exhibit a large degree of scatter at room temperature. While the most recent and lowest rate coefficient of Atkinson and Aschmann[6] may be the most accurate (any impurities would lead to higher rate constants), the preferred value and its associated large uncertainty cover the available 298 K rate coefficients. No recommendation is made regarding the temperature dependence. The preferred value is identical to our previous evaluation, IUPAC, 1992.[7]

References

[1] R. D. Cadle and C. Schadt, J. Phys. Chem. **21**, 163 (1953).

[2] W. B. DeMore, Int. J. Chem. Kinet. **1**, 209 (1969).

[illegible] H. DeMore, Int. J. Chem. Kinet. **3**, 161 (1971).
[illegible] H. Stedman and H. Niki, Environ. Lett. **4**, 303 (1973).
[illegible] Pate, R. Atkinson, and J. N. Pitts, Jr., J. Environ. Sci. Health **A11**, 1 (1976).
[6]R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **16**, 259 (1984).
[7]IUPAC, *Supplement IV*, 1992 (*see references in Introduction*).

$O_3 + C_2H_4 \rightarrow$ products

Rate coefficient data

[illegible] molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
[illegible]$\times 10^{-15}\exp[-(2446\pm91)/T]$	240–324	Treacy *et al.*, 1992[1]	(a)
([illegible]7$\pm$0.08)$\times 10^{-18}$	298		
Reviews and Evaluations			
[illegible]$\times 10^{-14}\exp(-2630/T)$	180–360	IUPAC, 1992[2]	(b)
[illegible]14$\times 10^{-15}\exp(-2580/T)$	178–362	Atkinson, 1994[3]	(c)
[illegible]$\times 10^{-14}\exp(-2630/T)$	180–360	NASA, 1994[4]	(b)

Comments

(a) Static system, with chemiluminescence detection of O_3.

(b) Based on the rate coefficient data of DeMore,[5] Stedman *et al.*,[6] Herron and Huie,[7] Japar *et al.*,[8,9] Toby *et al.*,[10] Su *et al.*,[11] Adeniji *et al.*,[12] Kan *et al.*,[13] Atkinson *et al.*,[14] and Bahta *et al.*[15]

(c) Based on a least-squares analysis of the rate coefficients of DeMore,[5] Stedman *et al.*,[6] Herron and Huie,[7] Japar *et al.*,[8,9] Toby *et al.*,[10] Atkinson *et al.*,[14] Bahta *et al.*,[15] and the 298 K rate coefficient of Treacy *et al.*[1]

Preferred Values

$k = 1.6\times10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.1\times10^{-15}\exp(-2580/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 180–360 K.

Reliability

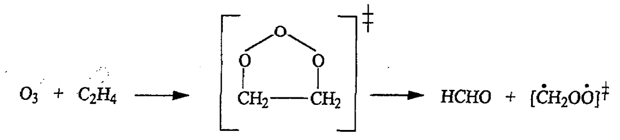
$\Delta\log k = \pm0.10$ at 298 K.

$\Delta(E/R) = \pm100$ K.

Comments on Preferred Values

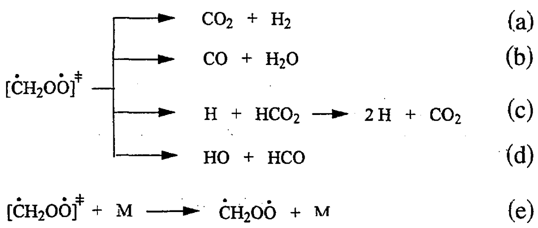
The most recent kinetic studies of Bahta *et al.*[15] and Treacy *et al.*[1] are in good agreement, and the rate coefficients from these studies[1,15] are somewhat lower than many of the previous rate coefficient data, including those of Su *et al.*[11] and Kan *et al.*[13] Since Treacy *et al.*[1] did not tabulate the individual rate coefficients at the various temperatures studied, only the 298 K rate constant can be used in the evaluation of the rate coefficient for this reaction. The preferred values are obtained from a least-squares analysis of the rate coefficients of DeMore,[5] Stedman *et al.*,[6] Herron and Huie,[7] Japar *et al.*,[8,9] Toby *et al.*,[10] Atkinson *et al.*,[14] Bahta *et al.*,[15] (averaging the rate coefficients at each of the four temperatures studied) and the 298 K rate coefficient of Treacy *et al.*[1]

As discussed by Atkinson and Lloyd,[16] Atkinson and Carter,[17] and Atkinson,[3] the initial reaction forms the energy-rich trioxane which rapidly decomposes:

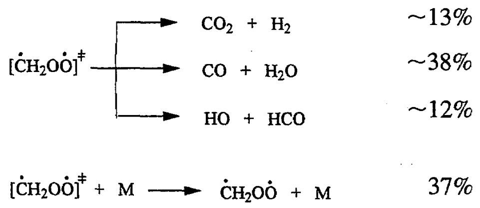


to yield HCHO and the energy-rich biradical $[\dot{C}H_2O\dot{O}]^{\ddagger}$.

This energy-rich biradical can either decompose or be stabilized



At room temperature and atmospheric pressure, the fraction of stabilization is ~0.37,[3,11,13,18–21] and is pressure dependent.[20] The fractions of the overall reactions proceeding via pathways (a) through (c) at room temperature and atmospheric pressure are then approximately 0.13, 0.31–0.58, and 0.06–0.10, respectively.[3] However, Atkinson *et al.*[22] have observed the formation of OH radicals at room temperature and atmospheric pressure of air, with a yield of ~0.12. The observed formation of OH radicals,[22] presumably via pathway (d), probably indicates that pathway (c) does not occur, since the study of Herron and Huie[23] could not differentiate between formation of H atoms and OH radicals (any H atoms formed would rapidly react with O_3 in the reaction system used by Herron and Huie[23] to produce OH radicals). Hence a possible reaction sequence is



The relative importance of these decomposition/stabilization reactions of the $[\dot{C}H_2O\dot{O}]^{\ddagger}$ radical are, however, pressure dependent,[20] with no quantitative data being available other than at ~1 bar of air.

References

[1] J. Treacy, M. El Hag, D. O'Farrell, and H. Sidebottom, Ber. Bunsenges. Phys. Chem. **96**, 422 (1992).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction)
[5] W. B. DeMore, Int. J. Chem. Kinet. **1**, 209 (1969).
[6] D. H. Stedman, C. H. Wu, and H. Niki, J. Phys. Chem. **77**, 2511 (1973).
[7] J. T. Herron and R. E. Huie, J. Phys. Chem. **78**, 2085 (1974)
[8] S. M. Japar, C. H. Wu, and H. Niki, J. Phys. Chem. **78**, 2318 (1974).
[9] S. M. Japar, C. H. Wu, and H. Niki, J. Phys. Chem. **80**, 2057 (1976).
[10] F. S. Toby, S. Toby, and H. E. O'Neal, Int. J. Chem. Kinet. **8**, 25 (1976).
[11] F. Su, J. G. Calvert, and J. H. Shaw, J. Phys. Chem. **84**, 239 (1980).
[12] S. A. Adeniji, J. A. Kerr, and M. R. Williams, Int. J. Chem. Kinet. **13**, 209 (1981).
[13] C. S. Kan, F. Su, J. G. Calvert, and J. H. Shaw, J. Phys. Chem. **85**, 2359 (1981).
[14] R. Atkinson, S. M. Aschmann, D. R. Fitz, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **14**, 13 (1982).
[15] A. Bahta, R. Simonaitis, and J. Heicklen, Int. J. Chem. Kinet. **16**, 1227 (1984).
[16] R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).
[17] R. Atkinson and W. P. L. Carter, Chem. Rev. **84**, 437 (1984).
[18] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **85**, 1024 (1981).
[19] S. Hatakeyama, H. Kobayashi, and H. Akimoto, J. Phys. Chem. **88**, 4736 (1984).
[20] S. Hatakeyama, H. Kobayashi, Z.-Y. Lin, H. Takagi, and H. Akimoto, J. Phys. Chem. **90**, 4131 (1986).
[21] O. Horie and G. K. Moortgat, Atmos. Environ. **25A**, 1881 (1991).
[22] R. Atkinson, S. M. Aschmann, J. Arey, and B. Shorees, J. Geophys. Res. **97**, 6065 (1992).
[23] J. T. Herron and R. E. Huie, J. Am. Chem. Soc. **99**, 5430 (1977).

$O_3 + C_3H_6 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.9\times10^{-15}\exp[-(1858\pm70)/T]$	240–324	Treacy *et al.*, 1992[1]	(a)
$(9.4\pm0.4)\times10^{-18}$	298		
Reviews and Evaluations			
$6.5\times10^{-15}\exp(-1880)/T)$	230–370	IUPAC, 1992[2]	(b)
$5.51\times10^{-15}\exp(-1878)/T)$	235–362	Atkinson, 1994[3]	(c)
$6.5\times10^{-15}\exp(-1900)/T)$	235–360	NASA, 1994[4]	(d)

Comments

(a) Static system, with chemiluminescence detection of O_3.

(b) Derived from a least-squares analysis of the absolute rate coefficient data of Cox and Penkett,[5] Stedman *et al.*,[6] Herron and Huie,[7] Japar *et al.*,[8,9] Adeniji *et al.*,[10] and Atkinson *et al.*[11]

(c) Derived from the absolute rate coefficient data of Herron and Huie[7] and Treacy *et al.*[1]

(d) Based mainly on the absolute rate coefficient data of Herron and Huie.[7]

Preferred Values

$k=1.0\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=5.5\times10^{-15}\exp(-1880/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–370 K.

Reliability

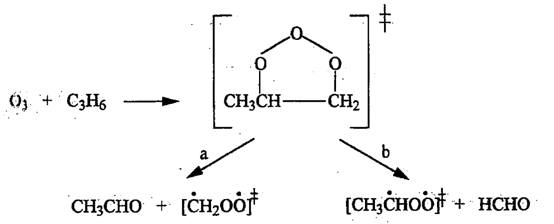
$\Delta\log k=\pm0.10$ at 298 K.

$\Delta(E/R)=\pm200$ K.

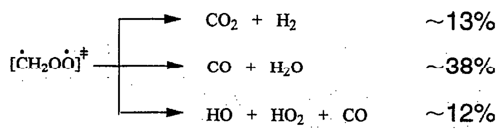
Comments on Preferred Values

The absolute rate coefficients of Herron and Huie[7] (note that the lowest temperature studied was 235.0 K and no 250.0 K as given by Herron and Huie[7]) and Treacy *et al.*[1] are in excellent agreement for propene, 1-butene, *cis*- and *trans*-2-butene, 2-methylpropene, and 2-methyl-2-butene over the temperature ranges common to both studies.[3] Accordingly the 298 K rate coefficients and temperature dependencies o Herron and Huie[7] and Treacy *et al.*[1] have been averaged to yield the preferred Arrhenius expression (note that the individual rate coefficients at the various temperatures studied b Treacy *et al.*[1] were not tabulated).

The reaction proceeds via the initial formation of a trioxane, which rapidly decomposes:

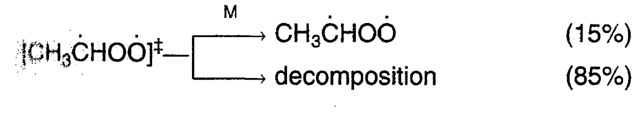


The rate coefficient ratio k_a/k_b has not been experimentally determined, and is assumed to be approximately unity although this is probably not the case.[12,13] It is generally assumed[14,15] that the reactions of the energy-rich biradical $[CH_2OO]^{\ddagger}$ formed from propene are similar to those for $[CH_2O\dot{O}]^{\ddagger}$ formed from ethene. Hence, as for the O_3+C_2H_4 reaction at room temperature and 1 bar of air

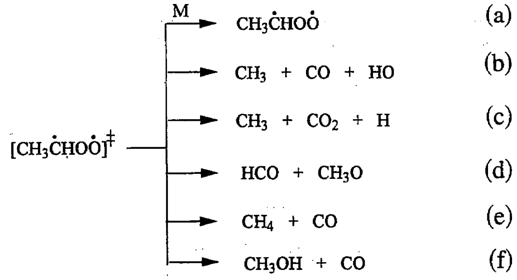


$$[\dot{C}H_2O\dot{O}]^{\ddagger} + M \longrightarrow CH_2O\dot{O} + M \qquad 37\%$$

Less data are available concerning the stabilization and decomposition reactions of the $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ biradical. Based upon the SO_2 to H_2SO_4 conversion yield in an O_3 + propene reaction system, Hatakeyama *et al.*[16] determined an overall stabilized biradical ($\dot{C}H_2O\dot{O}$+$CH_3\dot{C}HO\dot{O}$) yield of 0.254 ± 0.023 at room temperature and atmospheric pressure, while Horie and Moortgat[12] obtained a stabilized biradical yield of 0.44. Using the data of Hatakeyama *et al.*[16] and assuming that k_a=k_b and that the $[CH_2O\dot{O}]^{\ddagger}$ stabilization yield is 0.37, then the fraction of $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ biradicals which are stabilized at ~298 K and 1 bar of air is 0.14. While the stabilization/decomposition yields are expected to depend on the individual alkene reacting with O_3 (and on the total pressure and temperature), this fraction of $[CH_3\dot{C}HO\dot{O}]$ biradicals which are stabilized at 298 K and 1 bar of air is similar to the measured yields of stabilized $CH_3\dot{C}HO\dot{O}$ from *trans*-2-butene (0.185[16]) and *cis*-2-butene (0.18[17]). A yield of stabilized $CH_3\dot{C}HO\dot{O}$ from $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ of 0.15 at 298 K and 1 bar of air is recommended, consistent with the product data of Hatakeyama *et al.*[16]:

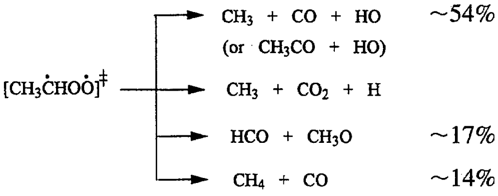


The decomposition pathways are less well understood,[12,14,15] but are expected to involve formation of CH_3 + CO + OH, CH_3 + CO_2 + H, HCO + CH_3O, CH_4 + CO_2, and CH_3OH + CO



Recent studies and evaluations[2,12] conclude that these channels have approximate fractional overall yields at ~1 bar of air of: channel (a) 0.15–0.42; channel (b), 0.16–0.30; channel (c), 0.17–0.34; channel (d), 0–0.07; channel (e), 0.14–0.17; and channel (f), 0–0.07. However, Atkinson and Aschmann[13] have observed the formation of OH radicals from the ozone reaction with propene at room temperature and atmospheric pressure of air, with a yield of 0.33 (uncertain to a factor of ~1.5). A possible reaction sequence for the $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ biradical at 298 K and 1 bar air is

$$[CH_3\dot{C}HO\dot{O}]^{\ddagger} + M \longrightarrow CH_3\dot{C}HO\dot{O} + M \qquad \sim 15\%$$



References

[1] J. Treacy, M. El Hag, D. O'Farrell, and H. Sidebottom, Ber. Bunsenges. Phys. Chem. **96**, 422 (1992).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] R. Atkinson, J. Phys. Chem. Ref. Data, Monograph **2**, 1 (1994).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] R. A. Cox and S. A. Penkett, J. Chem. Soc. Faraday Trans. 1, **68**, 1735 (1972).
[6] D. H. Stedman, C. H. Wu, and H. Niki, J. Phys. Chem. **77**, 2511 (1973).
[7] J. T. Herron and R. E. Huie, J. Phys. Chem. **78**, 2085 (1974).
[8] S. M. Japar, C. H. Wu, and H. Niki, J. Phys. Chem. **78**, 2318 (1974).
[9] S. M. Japar, C. H. Wu, and H. Niki, J. Phys. Chem. **80**, 2057 (1976).
[10] S. A. Adeniji, J. A. Kerr, and M. R. Williams, Int. J. Chem. Kinet. **13**, 209 (1981).
[11] R. Atkinson, S. M. Aschmann, D. R. Fitz, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **14**, 13 (1982).
[12] O. Horie and G. K. Moortgat, Atmos. Environ. **25A**, 1881 (1991).
[13] R. Atkinson and S. M. Aschmann, Environ. Sci. Technol. **27**, 1357 (1993).
[14] R. Atkinson and W. P. L. Carter, Chem. Rev. **84**, 437 (1984).
[15] R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).
[16] S. Hatakeyama, H. Kobayashi, and H. Akimoto, J. Phys. Chem. **88**, 4736 (1984).
[17] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Chem. Phys. Lett. **46**, 327 (1977).

HCHO + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
HCHO + $h\nu \rightarrow$ H + HCO (1)	363.8	329
$\rightarrow H_2$ + CO (2)	−1.9	-

Preferred Values

Absorption cross-sections for HCHO photolysis over the wavelength region 240–360 nm, T = 285 K[a]

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
240	0.064	271	1.789	302	1.064	333	0.215
241	0.056	272	1.227	303	3.201	334	0.171
242	0.105	273	0.645	304	6.902	335	0.143
243	0.115	274	0.656	305	4.914	336	0.194
244	0.082	275	2.232	306	4.632	337	0.417
245	0.103	276	2.416	307	2.100	338	2.360
246	0.098	277	1.402	308	1.494	339	4.712
247	0.135	278	1.050	309	3.407	340	2.481
248	0.191	279	2.548	310	1.950	341	0.759
249	0.282	280	2.083	311	0.521	342	0.681
250	0.205	281	1.475	312	1.120	343	1.953
251	0.170	282	0.881	313	1.116	344	1.137
252	0.288	283	1.066	314	4.747	345	0.323
253	0.255	284	4.492	315	5.247	346	0.113
254	0.255	285	3.592	316	2.899	347	0.066
255	0.360	286	1.962	317	5.373	348	0.122
256	0.509	287	1.295	318	2.975	349	0.032
257	0.339	288	3.356	319	0.918	350	0.038
258	0.226	289	2.838	320	1.262	351	0.104
259	0.504	290	1.304	321	1.529	352	0.713
260	0.505	291	1.746	322	0.669	353	2.212
261	0.549	292	0.832	323	0.345	354	1.536
262	0.520	293	3.727	324	0.816	355	0.676
263	0.933	294	6.535	325	1.850	356	0.135
264	0.823	295	3.950	326	5.950	357	0.036
265	0.430	296	2.333	327	3.485	358	0.0057
266	0.495	297	1.513	328	1.087	359	0.058
267	1.239	298	4.037	329	3.353	360	0.082
268	1.110	299	2.871	330	3.321		
269	0.878	300	0.871	331	1.073		
270	0.936	301	1.715	332	0.289		

[a] Averaged over 0.5 nm wavelength intervals centered at the cited wavelength [G. K. Moortgat and W. Schneider (unpublished data)].

Absorption cross-sections for HCHO photolysis over the wavelength region 301.25–356.25 nm[a] as a function of temperature (223–293 K)[b]

	σ/cm^2		*Intercept*	*Temp.*
λ/nm	223 K	293 K	(273 K)	gradient
301.25	1.38E-20	1.36E-20	1.37E-20	−2.10E-24
303.75	4.67E-20	4.33E-20	4.43E-20	−4.73E-23
306.25	3.32E-20	3.25E-20	3.27E-20	−1.06E-23
308.75	2.27E-20	2.22E-20	2.24E-20	−7.24E-24
311.25	7.58E-21	9.31E-21	8.82E-21	2.48E-23
313.75	3.65E-20	3.40E-20	3.47E-20	−3.64E-23
316.25	4.05E-20	3.89E-20	3.94E-20	−2.30E-23
318.75	1.66E-20	1.70E-20	1.69E-20	6.59E-24
321.25	1.24E-20	1.13E-20	1.16E-20	−1.52E-23
323.75	4.65E-21	4.73E-21	4.71E-21	1.18E-24
326.25	5.06E-20	4.44E-20	4.61E-20	−8.86E-23
328.75	2.44E-20	2.29E-20	2.43E-20	−2.15E-23
331.25	1.39E-20	1.28E-20	1.31E-20	−1.53E-23
333.75	9.26E-22	1.23E-21	1.14E-21	4.32E-24
336.25	1.27E-21	1.13E-21	1.30E-21	5.03E-25
338.75	3.98E-20	3.36E-20	3.45E-20	−8.96E-23
341.25	8.05E-21	9.36E-21	8.98E-21	1.86E-23
343.75	1.44E-20	1.26E-20	1.31E-20	−2.64E-23
346.25	3.39E-23	7.10E-22	5.18E-22	9.57E-24
348.75	9.05E-23	3.97E-22	3.10E-22	4.38E-24
351.25	1.69E-21	2.35E-21	2.16E-21	9.48E-24
353.75	1.83E-20	1.55E-20	1.63E-20	−4.05E-23
356.25	3.54E-22	1.25E-21	9.19E-22	1.27E-23

[a] 2.5 nm interval centered at given λ.

[b] At any temperature within the range 223–293 K, σ can be calculated from the listed gradient (slope) and intercept fit parameters, with σ=(slope ×T(°C)+intercept) [C. A. Cantrell, J. A. Davidson, A. H. McDaniel, R. E. Shetter, and J. G. Calvert, J. Phys. Chem. **94**, 3902 (1990)].

Quantum Yields for HCHO photolysis

λ/nm	ϕ_1	ϕ_2
240	0.27	0.49
250	0.29	0.49
260	0.30	0.49
270	0.38	0.43
280	0.57	0.32
290	0.73	0.24
300	0.78	0.21
310	0.78	0.22
320	0.62	0.38
330	0.27	0.66
340	0.00	0.56
350	0.00	0.21
360	0.00	0.03

Comments on Preferred Values

The preferred values are identical to our previous evaluation, 1992.[1] The recommended absorption cross-sections are those of Moortgat and Schneider[2] for $\lambda \leq 300$ nm and of Cantrell *et al.*[3] for $\lambda = 301-356$ nm, the latter providing a temperature dependence over the range 223–293 K.

The problem of understanding the measured quantum yields and branching ratios, $Y_2 = \phi_2/(\phi_1 + \phi_2)$, remains unresolved. If the photochemistry were governed by a sequence of light absorption into the first excited electronic state, internal conversion to the electronic ground state, and subsequent competition of the reactions $HCHO^* \rightarrow H + HCO$ and $HCHO^* \rightarrow H_2 + CO$, then the measured values of Y_2 for $\lambda \leq 300$ nm would be difficult to interpret. Simulations[4] of the rates of the competing processes of HCHO* and measurements of the product yields in molecular beams[5] indicates that the radical channel (1), $HCHO^* \rightarrow H + HCO$ dominates for $\lambda \leq 300$ nm, with $Y_2 < 0.1$ at 284 nm.[5] An analysis of the details of the photophysical processes[6] has failed to resolve this discrepancy with the macroscopic photochemical observations. The branching ratios for $\lesssim 300$ nm should therefore be treated with caution.

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).

[2] G. K. Moortgat and W. Schneider, unpublished data.

[3] C. A. Cantrell, J. A. Davidson, A. H. McDaniel, R. E. Shetter, and J. G. Calvert, J. Phys. Chem. **94**, 3902 (1990).

[4] J. Troe, J. Phys. Chem. **88**, 4375 (1984).

[5] P. Ho, D. J. Bamford, R. J. Buss, Y. T. Lee, and C. B. Moore, J. Chem. Phys. **76**, 3630 (1982).

[6] C. B. Moore and J. C. Weisshaar, Annu. Rev. Phys. Chem. **34**, 325 (1983).

$CH_3CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ · mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CHO + h\nu \rightarrow CH_4 + CO$	(1)	−19.5	
$\rightarrow CH_3 + HCO$	(2)	349.0	343
$\rightarrow CH_3CO + H$	(3)	359.5	333

Absorption cross-sections

Wavelength range/nm	Reference	Comments
202–365	Martinez *et al.*, 1992[1]	(a)

Comments

(a) Cross-sections are the average cross-section over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region centered at the corresponding wavelength (see Preferred Values).

Preferred Values

Absorption cross-sections for acetaldehyde

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2
202	0.056	297	4.38	334	0.363
206	0.053	298	4.41	335	0.350
210	0.049	299	4.26	336	0.238
214	0.048	300	4.16	337	0.222
218	0.052	301	3.99	338	0.205
222	0.065	302	3.86	339	0.219
226	0.096	303	3.72	340	0.150
230	0.151	304	3.48	341	0.074
234	0.241	305	3.42	342	0.042
238	0.375	306	3.42	343	0.031
242	0.564	307	3.36	344	0.026
246	0.818	308	3.33	345	0.021
250	1.128	309	3.14	346	0.019
254	1.524	310	2.93	347	0.015
258	1.994	311	2.76	348	0.016
262	2.44	312	2.53	349	0.010
266	3.05	313	2.47	350	0.008
270	3.42	314	2.44	351	0.007
274	4.03	315	2.20	352	0.006
278	4.19	316	2.04	353	0.005
280	4.50	317	2.07	354	0.005
281	4.69	318	1.979	355	0.004
282	4.72	319	1.874	356	0.005
283	4.75	320	1.723	357	0.003
284	4.61	321	1.484	358	0.004
285	4.49	322	1.402	359	0.002
286	4.44	323	1.244	360	0.003
287	4.59	324	1.091	361	0.002
288	4.72	325	1.136	362	0.001
289	4.77	326	1.074	363	0.000
290	4.89	327	0.858	364	0.000
291	4.78	328	0.747	365	0.000
292	4.68	329	0.707		
293	4.53	330	0.688		
294	4.33	331	0.588		
295	4.27	332	0.530		
296	4.24	333	0.398		

Quantum Yields for 1 atm air

λ/nm	ϕ_1	ϕ_2
260	0.46	0.31
270	0.31	0.39
280	0.05	0.58
290	0.01	0.53
295	0.00	0.48
300		0.43
305		0.37
315		0.17
320		0.10
325		0.04
330		0.00

Comments on Preferred Values

The preferred absorption cross-sections are from the recent more extensive measurements of Martinez *et al.*[1] Over the wavelength region 260–320 nm these cross-sections are within 5% of our previous recommendations based on the data of Calvert and Pitts[2] and Weaver *et al.*[3]

Our previous recommendations[4] for the quantum yield remain unaltered.

References

[1] R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn, and J. A. Joens, Atmos. Environ. **26A**, 785 (1992).

[2] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).

[3] J. Weaver, J. Meagher, and J. Heicklen, J. Photochem. **6**, 111 (1976).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$C_2H_5CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ · mol^{-1}	$\lambda_{\text{threshold}}$/nm
$C_2H_5CHO \rightarrow C_2H_5 + HCO$	(1)	343.1	349
$\rightarrow C_2H_6 + CO$	(2)	−7.1	
$\rightarrow C_2H_4 + HCHO$	(3)	131.0	913
$\rightarrow CH_3 + CH_2CHO$	(4)	336.4	356

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–365	Martinez *et al.*, 1992[1]	(a)

Comments

Cross-sections are the average cross-section over a 1 nm (λ>280 nm) or 4 nm (λ<280 nm) region centered at the corresponding wavelength (see Preferred Values).

Preferred Values

Absorption cross-sections for propanal

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
202	0.049	295	5.57	330	0.575
206	0.049	296	5.37	331	0.494
210	0.057	297	5.16	332	0.466
214	0.069	298	5.02	333	0.430
218	0.080	299	5.02	334	0.373
222	0.091	300	5.04	335	0.325
226	0.115	301	5.09	336	0.280
230	0.163	302	5.07	337	0.230
234	0.257	303	4.94	338	0.185
238	0.407	304	4.69	339	0.166
242	0.622	305	4.32	340	0.155
246	0.909	306	4.04	341	0.119
250	1.287	307	3.81	342	0.076
254	1.745	308	3.65	343	0.045
258	2.25	309	3.62	344	0.031
262	2.88	310	3.60	345	0.025
266	3.43	311	3.53	346	0.019
270	4.12	312	3.50	347	0.016
274	4.59	313	3.32	348	0.014
278	5.17	314	3.06	349	0.013
280	5.16	315	2.77	350	0.010
281	5.21	316	2.43	351	0.008
282	5.35	317	2.18	352	0.007
283	5.57	318	2.00	353	0.005
284	5.78	319	1.864	354	0.004
285	5.86	320	1.831	355	0.002
286	5.82	321	1.777	356	0.001
287	5.72	322	1.662	357	0.001
288	5.59	323	1.577	358	0.000
289	5.52	324	1.488	359	0.000
290	5.56	325	1.300	360	0.000
291	5.68	326	1.129	361	0.000
292	5.81	327	0.996	362	0.000
293	5.88	328	0.828	363	0.000
294	5.80	329	0.685	364	0.000
				365	0.000

Quantum Yields for 1 atm air

λ/nm	ϕ_1
294	0.89
302	0.85
313	0.50
325	0.26
334	0.15

Comments on Preferred Values

The preferred absorption cross-sections are from the recent more extensive measurements of Martinez *et al.*[1] Over the wavelength region 260–320 nm these cross-sections are within 5% of our previous recommendations based on the data of Calvert and Pitts.[2]

The preferred values of the quantum yields for the photodissociation yielding C_2H_5 radicals are taken from the study of Heicklen *et al.*,[3] and refer to photolysis in air at a total pressure of 1 atm. No explanation has been put forward to account for the large differences in the reported values of ϕ_1 as a function of wavelength.[3–5]

References

[1] R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn, and J. A. Joens, Atmos. Environ. **26A**, 785 (1992).

[2] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).

[3] J. Heicklen, J. Desai, A. Bahta, C. Harper, and R. Simonaitis, J. Photochem. **34**, 117 (1986).

[4] P. B. Shepson and J. Heicklen, J. Photochem. **18**, 169 (1982).

[5] P. B. Shepson and J. Heicklen, J. Photochem. **19**, 215 (1982).

$(CHO)_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$(CHO)_2 + h\nu \rightarrow H_2 + 2CO$	(1)	−9.1	
$\rightarrow 2HCO$	(2)	286.3	418
$\rightarrow HCHO + CO$	(3)	−7.2	

Preferred Values

Absorption cross-sections for glyoxal

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
230.5	0.30	390	3.14	427	10.76
235	0.30	391	3.45	428	16.65
240	0.42	392	3.25	429	4.06
245	0.57	393	2.23	430	5.07
250	0.84	394	2.64	431	4.87
255	1.15	395	3.04	432	4.06
260	1.45	396	2.64	433	3.65
265	1.88	397	2.44	434	4.06
270	2.30	398	3.25	435	5.07
275	2.60	399	3.04	436	8.12
280	2.87	400	2.84	437	5.28
285	3.33	401	3.25	438	10.15
290	3.18	402	4.46	439	7.71
295	3.33	403	5.28	440	24.76
300	3.60	404	4.26	441	8.12
305	2.76	405	3.05	442	6.09
310	2.76	406	3.05	443	7.51
312.5	2.88	407	2.84	444	9.34
315	2.30	408	2.44	445	11.37
320	1.46	409	2.84	446	5.28
325	1.15	410	6.09	447	2.44
327.5	0.30	411	5.27	448	2.84
330	0.00	412	4.87	449	3.86
335	0.00	413	8.32	450	6.09
340	0.00	414	7.51	451	10.96
345	0.00	415	8.12	452	12.18
350	0.00	416	4.26	453	23.95
355	0.00	417	4.87	454	17.05
360	0.23	418	5.89	455	40.60
365	0.30	419	6.70	456	10.14
370	0.80	420	3.86	457	1.63
375	1.03	421	5.68	458	1.22
380	1.72	422	5.28	459	0.41
382	1.57	423	10.55	460	0.41
384	1.49	424	6.09	461	0.20
386	1.49	425	7.31	462	0.00
388	2.87	426	11.77		

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation, IUPAC, 1992.[1] The preferred values listed above are taken from the results of Plum *et al.*[2] and are in good agreement with the earlier published data summarized by Calvert and Pitts.[3]

The selection of preferred quantum yields for the photolysis of glyoxal as a function of wavelength under atmospheric conditions must await further investigations. The "effective" quantum yield of ϕ=0.029 reported by Plum *et al.*[2] is valid only for the particular spectral distribution used in their study. This value of ϕ may be used to calculate the rates of photolyses of glyoxal under tropospheric conditions within the spectral region 325–470 nm. For the lower wavelength band in the troposphere it is recommended that the value ϕ=0.4, reported by Langford and Moore[4] at 308 nm, be used in such calculations.

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).

[2] C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., Environ. Sci. Technol. **17**, 479 (1983).

[3] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).

[4] A. O. Langford and C. B. Moore, J. Chem. Phys. **80**, 4211 (1984).

CH_3COCHO + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CH_3COCHO + h\nu \rightarrow CH_4 + 2CO$	(1)	−24.7	
$\rightarrow CH_3CO + HCO$	(2)	284.0	421
$\rightarrow CH_3CHO + CO$	(3)	−5.2	

Preferred Values

Absorption cross-sections for methylglyoxal between 225 and 410 nm, at 5 nm intervals

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
225	1.268	320	1.511
230	1.477	325	0.938
235	1.803	330	0.652
240	2.071	335	0.482
245	2.304	340	0.323
250	2.612	345	0.300
255	2.859	350	0.394
260	3.280	355	0.560
265	3.618	360	0.695
270	4.159	365	1.077
275	4.413	370	1.475
280	4.877	375	1.911
285	4.719	380	2.429
290	4.838	385	3.221
295	4.362	390	4.029
300	3.754	395	4.732
305	3.361	400	5.664
310	2.365	405	6.923
315	1.891	410	8.459

Preferred Values

Absorption cross-sections for methylglyoxal between 401 and 475 nm, at 1 nm intervals

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
401	5.90	439	11.01
402	6.07	440	9.94
403	6.35	441	10.39
404	6.54	442	10.20
405	6.91	443	10.17
406	7.20	444	11.17
407	7.58	445	9.61
408	7.94	446	8.90
409	8.12	447	9.84
410	8.52	448	9.18
411	8.63	449	10.13
412	9.07	450	8.67
413	9.37	451	6.34
414	9.62	452	6.33
415	9.68	453	6.08
416	9.71	454	4.46
417	10.04	455	3.69
418	10.07	456	3.08
419	10.12	457	2.46
420	10.21	458	1.81
421	10.34	459	1.28
422	10.51	460	0.914
423	10.45	461	0.795
424	10.15	462	0.642
425	10.34	463	0.479
426	10.24	464	0.332
427	9.84	465	0.268
428	10.01	466	0.227
429	9.94	467	0.187
430	10.41	468	0.160
431	10.53	469	0.133
432	9.79	470	0.108
433	10.64	471	0.099
434	10.54	472	0.089
435	10.81	473	0.077
436	11.13	474	0.067
437	9.99	475	0.062
438	10.59		

Comments on Preferred Values

The preferred values of the absorption cross-sections are identical to our previous evaluation, IUPAC, 1992.[1] The measurements of the cross-sections reported by Meller *et al.*[2] are approximately a factor of two higher than the previous measurements of Plum *et al.*[3] The data of Meller *et al.*[2] are preferred because of the agreement between the cross-sections measured by conventional spectroscopy and from *in situ* generation of methylglyoxal.[2] In addition, Meller *et al.*[2] found evidence of problems in the handling of methylglyoxal which were minimized by the *in situ* generation technique and which seem likely to have been present in the study of Plum *et al.*[3]

No further work has been reported on the quantum yields for the photolysis of methylglyoxal as a function of wavelength under atmospheric conditions. Plum *et al.*[3] measured the rate of photolysis of methylglyoxal, equal to $\int \sigma_\lambda \phi_\lambda J_\lambda \times d\lambda$. Hence the ''effective value of ϕ measured by Plum *et al.*[3] for the spectral range (325–475 nm) and distribution used[3] must be reduced by a factor of ~2 to be consistent with the increased values of σ now being recommended.

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).

[2] R. Meller, W. Raber, J. N. Crowley, M. E. Jenkin, and G. K. Moortgat, J. Photochem. Photobiol., A: Chemistry **62**, 163 (1991).

[3] C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., Environ. Sci. Technol. **17**, 479 (1983).

$CH_3COCH_3 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ · mol^{-1}	$\lambda_{threshold}$/nm
$CH_3COCH_3 + h\nu \rightarrow CH_3CO + CH_3$	(1)	338.9	353
$\rightarrow 2CH_3 + CO$	(2)	398.7	300

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–365	Martinez *et al.*, 1992[1]	(a)
260–360	Hynes *et al.*, 1992[2]	(b)

Comments

(a) Cross-sections are the average cross-section over a 1 nm ($\lambda>280$ nm) or 4 nm ($\lambda<280$ nm) region centered at the corresponding wavelength (see Preferred Values).

(b) Cross-sections measured as a function of temperature over the range 260–360 K. Data were presented in graphical form and show a marked decrease in cross-section with decreasing temperature.

Preferred Values

Absorption cross-sections for acetone

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
202	0.533	295	3.52	330	0.067
206	0.125	296	3.35	331	0.051
210	0.104	297	3.20	332	0.040
214	0.120	298	2.07	333	0.031
218	0.163	299	2.91	334	0.026
222	0.242	300	2.77	335	0.017
226	0.361	301	2.66	336	0.014
230	0.533	302	2.53	337	0.011
234	0.774	303	2.37	338	0.009
238	1.086	304	2.24	339	0.006
242	1.479	305	2.11	340	0.005
246	1.944	306	1.952	341	0.005
250	2.47	307	1.801	342	0.003
254	3.04	308	1.663	343	0.004
258	3.61	309	1.537	344	0.002
262	4.15	310	1.408	345	0.002
266	4.58	311	1.276	346	0.001
270	4.91	312	1.173	347	0.002
274	5.06	313	1.081	348	0.001
278	5.07	314	0.967	349	0.001
280	5.05	315	0.858	350	0.001
281	5.01	316	0.777	351	0.000
282	4.94	317	0.699	352	0.001
283	4.86	318	0.608	353	0.000
284	4.76	319	0.530	354	0.001
285	4.68	320	0.467	355	0.000
286	4.58	321	0.407		
287	4.50	322	0.344		
288	4.41	323	0.287		
289	4.29	324	0.243		
290	4.19	325	0.205		
291	4.08	326	0.168		
292	3.94	327	0.135		
293	3.81	328	0.108		
294	3.67	329	0.086		

Quantum Yields for 1 atm air

λ/nm	ϕ_1
250	0.76
260	0.80
270	0.64
280	0.55
290	0.30
300	0.15
310	0.05
320	0.028
330	0.033

Comments on Preferred Values

The preferred absorption cross-sections are from the recent extensive measurements of Martinez *et al.*[1] Over the wavelength region 260–320 nm these cross-sections are within 5% of our previous recommendations based on the data of Calvert and Pitts[3] and Meyrahn *et al.*[4] The cross-sections reported by Hynes *et al.*[2] at room temperature contain large error limits at 320 and 340 nm but are in reasonable agreement with those recommended here.

This latter study[2] has also shown that the cross-sections are temperature dependent. Since no easily presentable formulation of the effect of temperature on the cross-sections was given, the original paper[2] should be consulted for details. It was noted, however, that neglecting the temperature-dependence of the cross-sections results in significant overestimation of the photodissociation rates at lower temperature, by, for example, ~50% at 220 K in the upper troposphere.[2]

The two studies[4,5] of the photodissociation of acetone in air are not in agreement regarding the quantum yield measurements. As pointed out by Meyrahn *et al.*,[4] further work on this system is needed to elucidate more quantitative details such as the collisional deactivation of photoexcited acetone. In the meantime, we have recommended the quantum yield data of Meyrahn *et al.*,[4] on the basis that the trend in ϕ_1 with wavelength observed by these authors appears to be reasonable.

References

[1] R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn, and J. A. Joens, Atmos. Environ. **26A**, 785 (1992).

[2] A. J. Hynes, E. A. Kenyon, A. J. Pounds, and P. H. Wine, Spectrochim. Acta **48A**, 1235 (1992).

[3] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).

[4] H. Meyrahn, J. Pauly, W. Schneider, and P. Warneck, J. Atmos. Chem. **4**, 277 (1986).

[5] E. P. Gardner, R. D. Wijayaratne, and J. G. Calvert, J. Phys. Chem. **88**, 5069 (1986).

$CH_3OOH + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ·mol^{-1} [a]	$\lambda_{threshold}$/nm
$CH_3OOH + h\nu \rightarrow CH_3O + HO$ (1)	188	637
$\rightarrow CH_3 + HO_2$ (2)	292	410
$\rightarrow CH_3O_2 + H$ (3)	359	333

[a] Calculated assuming $\Delta H^\circ_0 = \Delta H^\circ_{298}$, C_p data are not available for CH_3OOH.

Preferred Values

Absorption cross-sections

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
210	31.2	290	0.691
215	20.9	295	0.551
220	15.4	300	0.413
225	12.2	305	0.313
230	9.62	310	0.239
235	7.61	315	0.182
240	6.05	320	0.137
245	4.88	325	0.105
250	3.98	330	0.079
255	3.23	335	0.061
260	2.56	340	0.047
265	2.11	345	0.035
270	1.70	350	0.027
275	1.39	355	0.021
280	1.09	360	0.016
285	0.863	365	0.012

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.[1] The preferred absorption cross-section data are those of Vaghjiani and Ravishankara,[2] which are approximately 25% lower than the previously recommended data of Molina and Arguello.[3] The source of the discrepancy appears to lie in the determination of the concentrations of CH_3OOH in the absorption cell. Molina and Arguello[3] used a bubbler containing Fe^{2+} solution, which Vaghjiani and Ravishankara[2] showed does not give quantitative trapping.

On the basis of the results of Vaghjiani and Ravishankara,[4] who showed that $\phi_{OH}{\sim}1.0$ at $\lambda=248$ nm, we recommend that for atmospheric photolysis of CH_3OOH, ϕ_1 be taken to be unity for wavelengths >290 nm.

References

[1] IUPAC, *Supplement IV*, 1992 (*see references in Introduction*).

[2] G. L. Vaghjiani and A. R. Ravishankara, J. Geophys. Res. **94**, 3487 (1989).

[3] M. J. Molina and G. Arguello, Geophys. Res. Lett. **6**, 953 (1979).

[4] G. L. Vaghjiani and A. R. Ravishankara, J. Chem. Phys. **92**, 996 (1990).

$CH_3ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ · mol^{-1}	$\lambda_{threshold}$/nm
$CH_3ONO_2 + h\nu \rightarrow CH_3O + NO_2$	(1)	170.5	702
$\rightarrow HCHO + HONO$	(2)	−68.4	
$\rightarrow CH_3ONO + O$	(3)	303.6	394

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–335	Rattigan *et al.*, 1992[1]	(a)

Comments

(a) Cross-sections were measured with a dual-beam diode array spectrometer with a spectral resolution of 0.3 nm over the temperature range 238–294 K. The temperature dependence of σ was found to obey the equation, $\log_{10}\sigma = \log_{10}\sigma_0 + BT$ with the following values of the intercept and slope of this equation:

λ/nm	10^{21} σ_0/cm^2	10^3 B/K^{-1}
270	8.91	1.41
280	4.92	1.70
290	2.18	2.00
300	0.62	2.58
310	0.129	3.23
320	0.0035	6.56
330	0.0004	7.38

Preferred Values at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$
270	2.37
275	1.99
280	1.57
285	1.17
290	0.836
295	0.559
300	0.356
305	0.211
310	0.139
315	0.0626
320	0.0312
325	0.0144
330	0.0066

Comments on Preferred Values

The preferred absorption cross-sections are the average values at room temperature from the data of Roberts and Fajer[2] and Rattigan *et al.*,[1] which are in reasonable agreement with the absorption spectrum reported by Calvert and Pitts[3] and with the cross-sections reported by Maria *et al.*[4] The results of Taylor *et al.*[5] are consistently higher than the values of the other four studies,[1–4] by as much as a factor of two in the region 290–330 nm. There is no apparent explanation of this discrepancy.[6] The effect of temperature on σ may be calculated from the expression reported by Rattigan *et al.*[1] and listed above.

The sole evidence on the primary processes comes from the study of Gray and Style,[7] who concluded from the products of photolyses that reaction (1) occurred, but reported no quantum yield data. It has generally been assumed[6] that the lack of structure in the absorption spectra of $RONO_2$ molecules indicates that the quantum yield for dissociation is unity. In the case of ethyl and propyl nitrates this conclusion is supported by experimental data on the rates of photolysis of the nitrates in sunlight (see comments on photolyses of other alkyl nitrates).

References

[1] O. Rattigan, E. Lutman, R. L. Jones, R. A. Cox, K. Clemitshaw, and J. Williams, J. Photochem. Photobiol. A: Chem. **66**, 313 (1992); *corrigendum, ibid.*, **69**, 125 (1992).
[2] J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).
[3] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).
[4] H. J. Maria, J. R. McDonald, and S. P. McGlynn, J. Am. Chem. Soc. **95**, 1050 (1973).
[5] W. D. Taylor, T. D. Allston, M. J. Moscato, G. B. Fazekas, R. Kozlowski, and G. A. Takacs, Int. J. Chem. Kinet. **12**, 231 (1980).
[6] J. M. Roberts, Atmos. Environ. **24A**, 243 (1990).
[7] J. A. Gray and D. W. G. Style, Trans. Faraday Soc. **49**, 52 (1953).

$C_2H_5ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H^\circ_{298}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$C_2H_5ONO_2 + h\nu \rightarrow C_2H_5O + NO_2$	(1)	170.0	704
$\rightarrow CH_3CHO + HONO$	(2)	−91.2	
$\rightarrow C_2H_5ONO + O$	(3)		

Preferred Values

λ/nm	$10^{20}\ \sigma/\text{cm}^2$	λ/nm	$10^{20}\ \sigma/\text{cm}^2$
185	1710	260	4.1
188	1760	265	3.7
190	1710	270	3.2
195	1490	275	2.8
200	1140	280	2.3
205	738	285	1.8
210	400	290	1.3
215	195	295	0.85
220	91	300	0.54
225	45	305	0.32
230	24	310	0.18
235	13	315	0.091
240	8.0	320	0.045
245	5.6	325	0.023
250	4.7	330	0.011
255	4.3		

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.[1] The preferred absorption cross-sections are from the measurements of Turberg *et al.*[2] over the wavelength region 185–265 nm, and are the average of the measurements of Roberts and Fajer[3] and of Turberg *et al.*[2] over the wavelength region 270–330 nm. These two studies[2,3] are in good agreement over the wavelength region 270–315 nm, but show variations in the cross-sections of up to a factor of two over the region 320–330 nm. The data of Calvert and Pitts[4] from 245 to 303 nm and of Kaya *et al.*[5] from 185 to 225 nm yield somewhat higher cross-sections than the preferred data.

There are insufficient definitive data to recommend values of the quantum yields. It seems likely, however, since the absorption spectra of organic nitrates are structureless continua, that the total primary quantum yields for dissociation are unity. Evidence for this conclusion comes from direct measurements of the rates of formation of NO_2 from the photolyses of ethyl nitrate in sunlight.[6,7] These agreed well with the calculated rates of photolysis based on measurements of the absorption cross-sections, solar irradiances, and an assumed value of $\phi_1 = 1$ throughout the region 290–340 nm.

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).

[2] M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P. Klingensmith, and G. A. Takacs, J. Photochem. Photobiol. **A51**, 281 (1990).

[3] J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).

[4] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966

[5] K. Kaya, K. Kuwata, and S. Nogakura, Bull. Chem. Soc. Jpn. **37**, 105 (1964).

[6] W. T. Luke and R. R. Dickerson, Geophys. Res. Lett. **15**, 1181 (1988).

[7] W. T. Luke, R. R. Dickerson, and L. J. Nunnermacker, J. Geophys. Res **94**, 14905 (1989).

n-$C_3H_7ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
n-$C_3H_7ONO_2 + h\nu \rightarrow n$-$C_3H_7O + NO_2$	(1)	165.9	721
$\rightarrow C_2H_5CHO + HONO$	(2)	−92.8	
$\rightarrow C_3H_7ONO + O$	(3)		

Preferred Values

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
185	1810	260	4.3
188	1830	265	4.0
190	1800	270	3.6
195	1600	275	3.0
200	1260	280	2.5
205	855	285	1.9
210	489	290	1.4
215	244	295	1.0
220	114	300	0.66
225	57	305	0.40
230	29	310	0.23
235	16	315	0.17
240	9.2	320	0.11
245	6.4	325	0.078
250	5.0	330	0.060
255	4.6		

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.[1] The preferred absorption cross-sections are from the measurements of Turberg *et al.*[2] over the wavelength region 185–265 nm and 315–330 nm, and are the average of the measurements of Roberts and Fajer[3] and of Turberg *et al.*[2] over the wavelength region 250–310 nm. These two studies[2,3] are in agreement except at the longest wavelengths where the cross-sections become small, and consequently must involve large error limits.

There are no data on either the products of photodissociation or the quantum yields. It seems likely, however, since the absorption spectra of organic nitrates are structureless continua, that the total primary quantum yields for dissociation will be unity. Evidence for this conclusion comes from direct measurements of the rate of formation of NO_2 from the photolyses of n-$C_3H_7ONO_2$ in sunlight.[4] These agreed well with the calculated rates of photolyses, based on measurements of the absorption cross-sections, solar irradiances and an assumed value of $\phi_1 = 1$ throughout the wavelength region 290–340 nm.

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).

[2] M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P. Klingensmith, and G. A. Takacs, J. Photochem. Photobiol. **A51**, 281 (1990).

[3] J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).

[4] W. T. Luke, R. R. Dickerson, and L. J. Nunnermacker, J. Geophys. Res. **94**, 14905 (1989).

i-$C_3H_7ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
i-$C_3H_7ONO_2 + h\nu \rightarrow C_3H_7O + NO_2$	(1)	171.7	697
$\rightarrow CH_3COCH_3 + HONO$	(2)	−105.9	
$\rightarrow i$-$C_3H_7ONO + O$	(3)		

Preferred Values

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
185	1790	260	4.9
188	1810	265	4.6
190	1790	270	4.1
195	1610	275	3.6
200	1260	280	2.9
205	867	285	2.3
210	498	290	1.7
215	247	295	1.2
220	117	300	0.81
225	58	305	0.52
230	31	310	0.32
235	18	315	0.19
240	11	320	0.11
245	7.0	325	0.061
250	5.7	330	0.037
255	5.2		

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.[1] The preferred absorption cross-sections are from the measurements of Turberg *et al.*[2] over the wavelength region 185–265 nm, and are the average of the measurements of Roberts and Fajer[3] and of Turberg *et al.*[2] over the wavelength region 270–330 nm. These two studies[2,3] are in good agreement except at the longest wavelengths where the cross-sections become small, and consequently must involve large error limits.

There are no data on either the products of photodissociation or the quantum yields. It seems likely, however, since the absorption spectra of organic nitrates are structureless continua, that the total primary quantum yields for dissociation will be unity. Evidence from measurements of the rate of formation of NO_2 from the photolyses of alkyl nitrates in sunlight supports this conclusion.[4] Thus the measured rates of formation of NO_2 matched well with calculated rates of photolyses of the $RONO_2$ based on measurements of the absorption cross-sections, solar irradiances and an assumed value of $\phi_1 = 1$ throughout the wavelength region 290–330 nm.

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).

[2] M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P. Klingensmith, and G. A. Takacs, J. Photochem. Photobiol. **A51**, 281 (1990).

[3] J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).

[4] W. T. Luke, R. R. Dickerson, and L. J. Nunnermacker, J. Geophys. Res. **94**, 14905 (1989).

$CH_3O_2NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ · mol^{-1} [a]	$\lambda_{threshold}$/nm
$CH_3O_2NO_2 + h\nu \rightarrow CH_3O_2 + NO_2$ (1)	88	1359
$\rightarrow CH_3O + NO_3$ (2)	126	949

[a] Only approximate values of ΔH°_{298} values are given since the heat of formation of $CH_3O_2NO_2$ is not well known.

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–280	Bridier, Lesclaux, and Veyret, 1992[1]	(a)

Comments

(a) Flash photolysis of Cl_2 in the presence of CH_4-O_2-NO_2 mixtures at a total pressure of 760 Torr, with UV absorption to monitor the concentrations of CH_3O_2 radicals and $CH_3O_2NO_2$.

Preferred Values

Absorption cross-sections for $CH_3O_2NO_2$

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	500	265	20.0
205	360	270	16.0
210	240	275	13.0
215	150	280	10.5
220	105	285	6.2
225	80	290	3.9
230	68	295	2.4
235	60	300	1.4
240	53	305	0.85
245	46	310	0.53
250	39	315	0.39
255	32	320	0.24
260	26	325	0.15

Comments on Preferred Values

In view of the thermal instability of $CH_3O_2NO_2$, the measurement of the cross-sections for $CH_3O_2NO_2$ presents considerable experimental problems. Nevertheless the recent measurements of Bridier *et al.*[1] are in moderately good agreement with previous data[2-4] at wavelengths <255 nm. At longer wavelengths the agreement is less good and the experimental data from Cox and Tyndall,[2] which are the only values extending into the wavelength region of importance for the atmosphere ($\lambda \geq 290$ nm), show large scatter. The preferred values given in the table for wavelengths >280 nm are based on a comparison with the spectrum of HO_2NO_2 (this evaluation).

There are no data to indicate the relative importance of the two photodissociation channels, and neither can be precluded on energetic grounds in the absorbing wavelength region. By analogy with other molecules containing the $-NO_2$ chromophore (for example, HNO_3), it is likely that absorption around 270 nm is associated with an orbitally forbidden n-π^* transition which leads to dissociation of the molecule. Thus it is probable that $\phi_1+\phi_2=1$.

References

[1] I. Bridier, R. Lesclaux, and B. Veyret, Chem. Phys. Lett. **191**, 259 (1992).
[2] R. A. Cox and G. S. Tyndall, Chem. Phys. Lett. **65**, 357 (1979).
[3] O. Morel, R. Simonaitis, and J. Heicklen, Chem. Phys. Lett. **73**, 38 (1980).
[4] S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).

$CH_3CO_3NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CH_3CO_3NO_2 + h\nu \rightarrow CH_3CO_3 + NO_2$ (1)	119	1005
$\rightarrow CH_3CO_2 + NO_3$ (2)	115	1040

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\phi(NO_2)$	248	Mazely, Friedl, and Sander, 1995[1]	(a)

Comments

(a) Pulsed laser photolysis of PAN with LIF detection of NO_2. The quantum yield for NO_2 formation was measured relative to that from the photodissociation of HNO_3 at 248 nm, assuming a value of $\phi(NO_2)$ from HNO_3 of unity at this wavelength (see data sheet for HNO_3 photolysis, this evaluation). A value of $\phi(NO_2)=0.83\pm0.09$ from the photolysis of PAN at 248 nm was obtained.

Preferred Values

Absorption cross-sections

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	317	255	7.9
205	237	260	5.7
210	165	265	4.04
215	115	270	2.79
220	77	275	1.82
225	55	280	1.14
230	39.9	285	0.716
235	29.0	290	0.414
240	20.9	295	0.221
245	15.9	300	0.105
250	10.9		

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Senum *et al.*,[2] which are in substantial agreement with the previously recommended provisional data,[3] and with the less direct measurements of Basco and Parmar.[4]

Measurements are still needed on the quantum yields and relative importance of the proposed primary processes as a function of wavelength. The NO_2 formation quantum yield measured by Mazely *et al.*[1] at 248 nm suggests that pathway (1) dominates. It is therefore suggested that $(\phi_1+\phi_2)=1$ for absorption in the UV region and that channel (1) forming CH_3CO_3 and NO_2 is the dominant photochemical primary process.

References

[1] T. L. Mazely, R. R. Friedl, and S. P. Sander, J. Phys. Chem. **99**, 8162 (1995).

[2] G. I. Senum, Y.-N. Lee, and J. S. Gaffney, J. Phys. Chem. **88**, 1269 (1984).

[3] CODATA, Supplement I, 1982 (see references in Introduction).

[4] N. Basco and S. S. Parmar, Int. J. Chem. Kinet. **19**, 115 (1987).

4.5 Sulfur Species

$O + CS \rightarrow CO + S$

$\Delta H^\circ = -355\ kJ \cdot mol^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 2.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.7 \times 10^{-10} \exp(-760/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 150–300 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

Because of its significance in the CO chemical laser, this reaction has been the subject of a number of studies.[1–4] The values of k obtained at 298 K fall within a range of about 20%. The preferred value is the mean of these measurements, all of which seem reliable. To obtain the preferred expression for k, the only available value of E/R is accepted and the pre-exponential factor is adjusted to fit the preferred value of k at 298 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[5]

References

[1] I. R. Slagle, R. E. Graham, J. R. Gilbert, and D. Gutman, Chem. Phys. Lett. **32**, 184 (1975).
[2] G. T. Bida, W. H. Breckenridge, and W. S. Kolln, J. Chem. Phys. **64**, 3296 (1976).
[3] H. V. Lilenfeld and R. J. Richardson, J. Chem. Phys. **67**, 3991 (1977).
[4] G. Hancock and I. W. M. Smith, Trans. Faraday Soc. **67**, 2586 (1971).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O + CH_3SCH_3 \rightarrow CH_3SO + CH_3$

$\Delta H^\circ = -133\ kJ \cdot mol^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 5.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3 \times 10^{-11} \exp(409/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–560 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The data of Nip *et al.*[1] are in excellent agreement, over the whole temperature range, with both of the studies of Lee *et al.*[2,3] The preferred values of k at 298 K and (E/R) are obtained from a least-squares fit of the data from those three studies and are identical to those in our previous evaluation, IUPAC, 1992.[4] The product study of Cvetanovic *et al.*[5] suggests that at high pressures (0.39–1.58 bar) the reaction proceeds almost entirely by addition followed by rapid fragmentation to $CH_3 + CH_3SO$.

References

[1] W. S. Nip, D. L. Singleton, and R. J. Cvetanovic, J. Am. Chem. Soc. **103**, 3526 (1981).
[2] J. H. Lee, R. B. Timmons, and L. J. Stief, J. Chem. Phys. **64**, 300 (1976).
[3] J. H. Lee, I. N. Tang, and R. B. Klemm, J. Chem. Phys. **72**, 1793 (1980).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).
[5] R. J. Cvetanovic, D. L. Singleton, and R. S. Irwin, J. Am. Chem. Soc. **103**, 3530 (1981).

$O + CS_2 \rightarrow SO + CS$ (1)
$\rightarrow CO + S_2$ (2)
$\rightarrow OCS + S$ (3)

$\Delta H^\circ(1) = -89\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta H^\circ(2) = -348\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta H^\circ(3) = -231\ \mathrm{kJ \cdot mol^{-1}}$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Branching Ratios			
$k_2/k = 0.030 \pm 0.010$	296	Cooper and Herschberger, 1992[1]	(a)
$k_3/k = 0.085 \pm 0.010$	296		
Reviews and Evaluations			
$3.2 \times 10^{-11} \exp(-650/T)$	200–500	IUPAC, 1992[2]	(b)
$3.2 \times 10^{-11} \exp(-650/T)$	200–300	NASA, 1994[3]	(c)

Comments

(a) Pulsed laser photolysis at 355 nm of NO_2-CS_2-SF_6 mixtures. CO and OCS were monitored by an infra-red diode laser absorption system, and concentrations were calculated using literature values of absorption linestrengths. Total $O(^3P)$ produced was obtained from the NO_2 absorption coefficient and dissociation quantum yield.

(b) See Comments on Preferred Values.

(c) Based on the work of Westenberg and deHaas,[4] Callear and Hedges,[5] Slagle *et al.*,[6] Wei and Timmons,[7] Graham and Gutman,[8] Callear and Smith,[9] and Homann *et al.*[10]

Preferred Values

$k = 3.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.2 \times 10^{-11} \exp(-650/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–500 K.
$k_1/k \geqslant 0.90$ over the temperature range 200–500 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

There are several determinations of k at 298 K using a variety of techniques, which are in good agreement. The preferred value is an average of the values of Westenberg and deHaas,[4] Callear and Hedges,[5] Slagle *et al.*,[6] Wei and Timmons,[7] Graham and Gutman,[8] Callear and Smith,[9] and Homann *et al.*[10] The preferred temperature coefficient is that of Wei and Timmons.[7] There is evidence to suggest that the Arrhenius plot is not linear over a wide temperature range but over the range for which our preferred values apply the other studies of the temperature dependence of k[8,10] are in good agreement with the value of Wei and Timmons.[7]

The reported values for the branching ratios show considerable scatter. For k_3/k values of 0.085,[1] 0.015,[12] 0.30,[13] 0.006,[14] and 0.093[6] have been reported and for k_2/k_1 values of 0.03,[1] 0.006,[14] 0.014,[11] and 0.05–0.20.[6] Channel 1 is clearly the major channel but at this stage our only recommendation is that $k_1/k \geqslant 0.90$.

References

[1] W. F. Cooper and J. F. Herschberger, J. Phys. Chem. **96**, 5405 (1992).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] A. A. Westenberg and N. deHaas, J. Chem. Phys. **50**, 707 (1969).
[5] A. B. Callear and R. E. M. Hedges, Trans. Faraday Soc. **66**, 605 (1970).
[6] I. R. Slagle, J. R. Gilbert, and D. Gutman, J. Chem. Phys. **61**, 704 (1974).
[7] C. N. Wei and R. B. Timmons, J. Chem. Phys. **62**, 3240 (1975).
[8] R. E. Graham and D. Gutman, J. Phys. Chem. **81**, 207 (1977).
[9] A. B. Callear and I. W. M. Smith, Nature **213**, 382 (1967).
[10] K. H. Homann, G. Krome, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **72**, 998 (1968).
[11] D. S. Y. Hsu, W. M. Shaub, T. L. Burks, and M. C. Lin, Chem. Phys. Lett. **44**, 143 (1979).
[12] G. Hancock and I. W. M. Smith, Trans. Faraday Soc. **67**, 2586 (1971).
[13] R. D. Stuart, P. H. Dawson, and G. H. Kimball, J. Appl. Phys. **81**, 207 (1977).
[14] V. L. Talrose, N. I. Butkovskaya, M. N. Larichev, I. O. Leipintskii, I. I. Morozov, A. F. Dodonov, B. V. Kudrov, V. V. Zelenov, and V. V. Raznikov, Adv. Mass Spectrom. **7**, 693 (1978).

$O + CH_3SSCH_3 \rightarrow CH_3SO + CH_3S$

$\Delta H° = -167$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.5 \times 10^{-11} \exp(250/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–570 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The data of Nip *et al.*[1] using a modulated photolysis technique are about a factor of 2 lower than the data from the earlier discharge flow-resonance fluorescence study of Lee *et al.*,[2] who reported no temperature dependence over the rather limited range 270–329 K. The cause of the discrepancy between the two measurements is not clear. The preferred value at 298 K is an average of the values from the two studies.[1,2] The temperature dependence is that from Nip *et al.*[1] with the A factor adjusted to yield the preferred value at 298 K. The preferred values are identical to our previous evaluation, IUPAC, 1992.[3]

The product study of Cvetanovic *et al.*[4] suggests that at high pressures, 0.39–1.58 bar, the reaction proceeds mainly by addition followed by rapid fragmentation to CH_3S + CH_3SO.

References

[1] W. S. Nip, D. L. Singleton, and R. J. Cvetanovic, J. Am. Chem. Soc. **103**, 3526 (1981).
[2] J. H. Lee, I. N. Tang, and R. B. Klemm, J. Chem. Phys. **72**, 5718 (1980).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] R. J. Cvetanovic, D. L. Singleton, and R. S. Irwin, J. Am. Chem. Soc. **103**, 3530 (1981).

$O + OCS \rightarrow SO + CO \quad (1)$
$\rightarrow CO_2 + S \quad (2)$

$\Delta H°(1) = -213$ kJ·mol^{-1}
$\Delta H°(2) = -224$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.6 \times 10^{-11} \exp(-2150/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–500 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The values obtained for k by a variety of techniques[1–9] are in excellent agreement over a wide range of temperatures, and pressures ($\leq$340 mbar). The available evidence suggests that at low temperatures the reaction proceeds by channel (1) and that channel (2) may only become significant at temperatures above 600 K.

Because of the possible enhancement of the rate by channel 2 at high temperatures, the recommended value of E/R is the mean of the values obtained in studies by Wei and Timmons[7] and Klemm and Stief[6] which were limited to temperatures below 502 K. The value of k at 298 K is the mean of the values in Refs. 1–9, and the pre-exponential factor is adjusted to fit this value of k and the recommended value of E/R. The preferred values are identical to our previous evaluation, IUPAC, 1992.[10]

Approximate values of k_2/k_1 measured are: 10^{-3} at 298 K[11] and 10^{-2} at 500 K.[3]

References

[1] J. O. Sullivan and P. Warneck, Ber. Bunsenges. Phys. Chem. **69**, 7 (1965).
[2] K. Hoyerman, H. Gg. Wagner, and J. Wolfrum, Ber. Bunsenges. Phys. Chem. **71**, 603 (1967).
[3] K. H. Homann, G. Krome, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **72**, 998 (1968).
[4] A. A. Westenberg and N. deHaas, J. Chem. Phys. **50**, 707 (1969).
[5] W. H. Breckenridge and T. A. Miller, J. Chem. Phys. **56**, 465 (1972).
[6] R. B. Klemm and L. J. Stief, J. Chem. Phys. **61**, 4900 (1974).
[7] C. N. Wei and R. B. Timmons, J. Chem. Phys. **62**, 3240 (1975).
[8] R. G. Manning, W. Braun, and M. J. Kurylo, J. Chem. Phys. **65**, 2609 (1976).
[9] N. Yoshida and S. Saito, Bull. Chem. Soc. Jpn. **51**, 1635 (1978).
[10] IUPAC, Supplement IV, 1992 (see references in Introduction).
[11] S. Dondes and P. Safrany, reported in Ref. 1.

$O + SO_2 + M \rightarrow SO_3 + M$

$\Delta H^\circ = -348.1$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.4 \times 10^{-33}$ [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.
$k_0 = 4.0 \times 10^{-32} \exp(-1000/T)$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability
$\Delta \log k_0 = \pm 0.3$ at 300 K.
$\Delta (E/R) = \pm 200$ K over the temperature range 200–400 K.

Comments on Preferred Values
The preferred values are based on the data from Ref. 1, the high temperature dissociation results from Ref. 2, and the theoretical analysis from Ref. 3. Because the reaction has an activation barrier, the Arrhenius form is chosen. The falloff transition to the high pressure range is expected at pressures not too far above 1 bar. However, no experimental data are available in this pressure region. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] R. Atkinson and J. N. Pitts, Jr., Int. J. Chem. Kinet. **10**, 1081 (1978).
[2] D. C. Astholz, G. Glänzer, and J. Troe, J. Chem. Phys. **70**, 2409 (1979).
[3] J. Troe, Ann. Rev. Phys. Chem. **29**, 223 (1978).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$S + O_2 \rightarrow SO + O$

$\Delta H^\circ = -23.0$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 2.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 230–400 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values
All of the available measurements of k are in good agreement. Clyne and Whitefield[1] found a small decrease in k with increase in temperature, but until more definitive measurements of E/R are made a temperature independent k is recommended with error limits encompassing the existing measured values. The preferred value at 298 K is the mean of values from Refs. 1–6, and is identical to our previous evaluation, IUPAC, 1992.[7]

References

[1] M. A. A. Clyne and P. D. Whitefield, J. Chem. Soc. Faraday Trans. 2, **75**, 1327 (1979).
[2] R. W. Fair and B. A. Thrush, Trans. Faraday Soc. **65**, 1557 (1969).
[3] R. W. Fair, A. Van Roodselaar, and O. P. Strausz, Can. J. Chem. **49**, 1659 (1971).
[4] D. D. Davis, R. B. Klemm, and M. J. Pilling, Int. J. Chem. Kinet. **4**, 367 (1972).
[5] R. J. Donovan and D. J. Little, Chem. Phys. Lett. **13**, 488 (1972).
[6] M. A. A. Clyne and L. W. Townsend, Int. J. Chem. Kinet. Symp. **1**, 73 (1975).
[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$S + O_3 \rightarrow SO + O_2$

$\Delta H^\circ = -414.9$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only available experimental determination[1] is accepted as the preferred value. The method was direct, and in the same study[1] a number of other rate coefficients for atom reactions were measured giving results in good agreement with other techniques. The preferred value is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] M. A. A. Clyne and L. W. Townsend, Int. J. Chem. Kinet. **Symp.** 1 (1975).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + H_2S \rightarrow HCl + HS$

$\Delta H^\circ = -50.0$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 210–350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

There is a significant scatter in the results which is difficult to attribute to any of the different techniques used. The preferred value at 298 K is a mean of the values of Nesbitt and Leone,[1] Clyne and Ono,[2] Clyne *et al.*,[3] and Nava *et al.*[4] The result of Lu *et al.*[5] is not included because of the very different conditions used. Both studies in which the temperature was varied[4,5] find a temperature coefficient of zero which is accepted but with substantial error limits. The preferred values are identical to our previous evaluation IUPAC, 1992.[6]

References

[1] D. J. Nesbitt and S. R. Leone, J. Chem. Phys. **72**, 1722 (1980).
[2] M. A. A. Clyne and Y. Ono, Chem. Phys. Lett. **94**, 597 (1983).
[3] M. A. A. Clyne, A. J. MacRobert, T. P. Murrells, and L. J. Stief, J. Chem. Soc. Faraday Trans. 2, **80**, 877 (1984).
[4] D. F. Nava, W. D. Brobst, and L. J. Stief, J. Phys. Chem. **89**, 4703 (1985).
[5] E. C. C. Lu, R. S. Iyer, and F. S. Rowland, J. Phys. Chem. **90**, 198 (1986).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + H_2S \rightarrow H_2O + HS$

$\Delta H^\circ = -117.5$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 4.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.3 \times 10^{-12} \exp(-80/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta (E/R) = \pm 80$ K.

Comments on Preferred Values

The data of Lin *et al.*,[1] Lafage *et al.*,[2] and Leu and Smith[3] are in good agreement and show that k exhibits non-Arrhenius behavior over the temperature range 245–450 K with the Arrhenius plot appearing to have a shallow minimum at approximately 270–300 K. Leu *et al.*[3] and Lin *et al.*[1] find that the value of k appears to be independent of pressure and nature of the bath gas. These latter results throw some doubt upon the suggestion that the non-Arrhenius behavior is due to the occurrence of both addition and abstraction channels.

Despite the non-Arrhenius behavior of k over an extended temperature range, the preferred expression is given in Arrhenius from, which is satisfactory for the limited temperature range covered by our recommendation. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] [illegible] Lin, N.-S. Wang, and Y.-P. Lee, Int. J. Chem. Kinet. 17, 1201 (1985).
[2] C. Lafage, J-F. Pauwels, M. Carlier, and P. Devolder, J. Chem. Soc. Faraday Trans. 2, **83**, 731 (1987).
[3] M.-T. Leu and R. H. Smith, J. Phys. Chem. **86**, 73 (1982).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + SO_2 + M \rightarrow HOSO_2 + M$

$\Delta H^\circ = -127$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 4.0 \times 10^{-31}$ $(T/300)^{-3.3}$ $[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–400 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The most recent measurements of Ref. 1 gave smaller rate coefficients than earlier studies. We included these values in the averaging of data which lead to the preferred values. The error limits encompass most of the earlier data. The difference in F_c values between Refs. 2 and 3, which leads to different k_0 and k_∞ values, should be noted.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

See comment to k_0. Falloff representation with $F_c = 0.45$ near 300 K. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] Y.-Y. Lee, W.-C. Kao, and Y.-P. Lee, J. Phys. Chem. **94**, 4535 (1990).
[2] IUPAC, Supplement III, 1989 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$

$\Delta H^\circ = 4$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 4.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.3 \times 10^{-12} \exp(-330/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–420 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

In the earlier studies[1,2] HO radical decays due to the reaction $HO + SO_2 + M \rightarrow HOSO_2 + M$ were monitored in the presence of NO and O_2. The reaction sequence $HOSO_2 + O_2 \rightarrow HO_2 + SO_3$ and $HO_2 + NO \rightarrow HO + NO_2$ then regenerates HO. Modeling of the NO decay leads to the rate coefficient k. This method of determining k is less direct than the more recent measurements of Gleason *et al.*[3] and Gleason and Howard[4] where $HOSO_2$ radicals were monitored by

MS. We therefore accept the expression obtained by Gleason and Howard.[4] The other results, though less precise, are in good agreement with the preferred expression. The preferred values are identical to our previous evaluation, IUPAC, 1992.[5]

References

[1] J. J. Margitan, J. Phys. Chem. **88**, 3314 (1984).
[2] D. Martin, J. L. Jourdain, and G. Le Bras, J. Phys. Chem. **90**, 4143 (19
[3] J. F. Gleason, A. Sinha, and C. J. Howard, J. Phys. Chem. **91**, 719 (19
[4] J. F. Gleason and C. J. Howard, J. Phys. Chem. **92**, 3414 (1988).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + OCS \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=2.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=1.1\times10^{-13}\exp(-1200/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–500 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

Values of k measured by Cheng and Lee[1] and by Wahner and Ravishankara[2] are approximately a factor of 3 lower at 298 K than the earlier value of Leu and Smith.[3] This may be due to the corrections applied by Leu and Smith[3] to account for the presence of traces of H_2S in their system since in the absence of such corrections there is reasonable agreement between the studies. Cheng and Lee[1] took care to keep the H_2S level in their OCS very low and this, together with the confirmatory measurements of Wahner and Ravishankara,[2] leads us to recommend their values. These recommendations are compatible with the earlier upper limit given by Atkinson *et al.*[4] but not with the higher value obtained by Kurylo[5] which may be due to interfering secondary chemistry and/or excited state reactions. The preferred values are identical to our previous evaluation, IUPAC, 1992.[6]

Kurylo and Laufer[7] have suggested that the reaction proceeds through adduct formation, as found for the reaction of HO with CS_2, followed by decomposition of the adduct to yield mainly HS + CO_2. There is some support for this from the product study of Leu and Smith.[3] However, in contrast to the HO + CS_2 reaction, there is no marked effect of O_2 on the rate. Furthermore, very little oxygen atom exchange between $H^{18}O$ and OCS is found[8] which may suggest that any adduct formed is weakly bound and short lived.

References

[1] B.-M. Cheng and Y.-P. Lee, Int. J. Chem. Kinet. **18**, 1303 (1986).
[2] A. Wahner and A. R. Ravishankara, J. Geophys. Res. **92**, 2189 (1987).
[3] M. T. Leu and R. H. Smith, J. Phys. Chem. **85**, 2570 (1981).
[4] R. Atkinson, R. A. Perry, and J. N. Pitts, Jr., Chem. Phys. Lett. **54**, 14 (1978).
[5] M. J. Kurylo, Chem. Phys. Lett. **58**, 238 (1978).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).
[7] M. J. Kurylo and A. H. Laufer, J. Chem. Phys. **70**, 2032 (1979).
[8] G. D. Greenblatt and C. J. Howard, J. Phys. Chem. **93**, 1035 (1989).

$HO + CS_2 + M \rightarrow HOCS_2 + M$ (1)
$HO + CS_2 \rightarrow HS + OCS$ (2)

$\Delta H^\circ(1)=-46.0$ kJ·mol^{-1}
$\Delta H^\circ(2)=-155$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{01}=8\times10^{-31}[N_2]$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 270–300 K.

Reliability

$\Delta\log k_{01}=\pm0.5$.

Comments on Preferred Values

Because of the low thermal stability of $HOCS_2$, experimental studies have to account for the redissociation of the adduct. After clarification of the mechanism, rate coefficients now can be specified. Combining the data for $M=N_2$ from Refs. 1 and 2 in a falloff representation indicates that the low pressure limit is approached within 10% only at pressures below about 20 Torr. Because of the rather large scatter, the falloff data do not yet allow for the specification of a temperature dependence. The strong temperature dependence of k_{01} for M=He derived in Ref. 3 ($E/R=-1610$ K) is apparently not consistent with the results from Refs. 1 and 2. It appears that reaction (2) is slow, with a rate coefficient of $k_2<2\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty 1}=8\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–300 K.

Reliability

$\Delta\log k_{\infty 1}=\pm0.5$ over the temperature range 250–300 K.

Comments on Preferred Values

The preferred rate coefficient $k_{\infty 1}$ is based on a falloff representation of the data from Refs. 1 and 2, with high-pressure data mostly from Ref. 1. The largest weight is given to the measurements near 250 K where decomposition of the adduct and the subsequent kinetics are of comparably minor influence in contrast to the room temperature experiments. A falloff curve with an estimated value of $F_c=0.8$ was employed for extrapolation. Experiments at 1 bar total pressure are apparently still far below the high-pressure limit. An extensive discussion of the complicated mechanism is given in Refs. 4–6 as well as in Refs. 1, 2, and 7. Rate expressions combining adduct formation, dissociation, and subsequent reactions with O_2 have been proposed which are not reproduced here. More experiments separating the individual steps are required. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[8]

References

[1] A. J. Hynes, P. H. Wine, and J. M. Nicovich, J. Phys. Chem. **92**, 3846 (1988).

[2] T. P. Murrells, E. R. Lovejoy, and A. R. Ravishankara, J. Phys. Chem. **94**, 2381 (1990).

[3] E. W.-G. Diau and Y.-P. Lee, J. Phys. Chem. **95**, 379 (1991).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

[5] CODATA, Supplement II, 1984 (see references in Introduction).

[6] IUPAC, Supplement III, 1989 (see references in Introduction).

[7] E. R. Lovejoy, T. P. Murrells, A. R. Ravishankara, and C. J. Howard, J. Phys. Chem. **94**, 2386 (1990).

[8] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HOCS_2 + M \rightarrow HO + CS_2 + M$

$\Delta H^\circ=46.0$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0=4.8\times10^{-14}$ [N_2] s^{-1} at 298 K.

$k_0=1.6\times10^{-6}\exp(-5160/T)$ [N_2] s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta\log k_0=\pm0.5$ at 298 K.

$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The preferred values are based on a falloff representation from Refs. 1 and 2 of the data for the reverse process $HO + CS_2 + M \rightarrow HOCS_2 + M$ and the determination of the equilibrium constant from the same work. Largest weight is given to the data from Ref. 2 which extend to lower pressures. The data from Ref. 3 are not consistent with this evaluation (with differences of about a factor of 2). $HOCS_2$ formation and dissociation are characterized by an equilibrium constant of $K_c=5.16\times10^{-25}\exp(5160/T)$ cm^3 molecule^{-1}, as derived from the data of Ref. 2.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 4.8 \times 10^5$ s^{-1} at 298 K.
$k_\infty = 1.6 \times 10^{13} \exp(-5160/T)$ s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are based on the falloff extrapolation of the data for the reverse reaction and the equilibrium constant $K_c = 5.16 \times 10^{-25} \exp(5160/T)$ cm^3 $molecule^{-1}$ from Ref. 2. Falloff curves are constructed with an estimated value of $F_c = 0.8$. The small pre-exponential factor of k_∞ can be explained theoretically as being due to the low bond energy of $HOCS_2$. For discussion of the mechanism, see Refs. 1, 2 and 4–7. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[8]

References

[1] A. J. Hynes, P. H. Wine, and J. M. Nicovich, J. Phys. Chem. **92**, 3846 (1988).
[2] T. P. Murrells, E. R. Lovejoy, and A. R. Ravishankara, J. Phys. Chem. 94 2381 (1990).
[3] E. W.-G. Diau and Y.-P. Lee, J. Phys. Chem. **95**, 379 (1991).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] CODATA, Supplement II, 1984 (see references in Introduction).
[6] IUPAC, Supplement III, 1989 (see references in Introduction).
[7] E. R. Lovejoy, T. P. Murrells, A. R. Ravishankara, and C. J. Howard, J. Phys. Chem. **94**, 2386 (1990).
[8] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HOCS_2 + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.1 \pm 0.6) \times 10^{-14}$	298	Diau and Lee, 1991[1]	(a)
Reviews and Evaluations			
2.8×10^{-14}	240–300	IUPAC, 1992[2]	(b)
See comment	200–300	NASA, 1994[3]	(c)

Comments

(a) Pulsed laser photolysis of H_2O_2 or HNO_3 at 248 nm in He-CS_2 mixtures. Pressure range 26–202 Torr. [HO] monitored by LIF. Values of $k(HOCS_2 + NO) = (7.3 \pm 1.8) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} and $k(HOCS_2 + NO_2) = (4.2 \pm 1.0) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} were also obtained in this work. The latter is the first measurement of the rate coefficient for the reaction with NO_2. The value for the reaction with NO is in good agreement with that of Lovejoy *et al.*[4]

(b) See Comments on Preferred Values.

(c) Overall reaction between HO and CS_2 considered. Expression of Hynes *et al.*[5] recommended (see Comments on Preferred Values).

Preferred Values

$k = 3.0 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, independent of temperature over the range 240–350 K.

Reliability

$\Delta \log k = \pm 0.3$ over the temperature range 240–350 K.

Comments on Preferred Values

The reaction of $HOCS_2$ with O_2 is an intermediate step in the overall reaction of HO with CS_2 under atmospheric conditions. The $HOCS_2$ is formed by the addition of HO to CS_2; once formed it may undergo dissociation back to HO and CS_2 or react with O_2. In previous evaluations, the $HOCS_2 + O_2$ reaction has been considered on the data sheet for HO + CS_2 because only in recent studies has the mechanism of the HO + CS_2 reaction been clarified and the individual reactions involved studied separately.

The three studies[1,5,6] of the kinetics of this reaction are in good agreement. Basically the same technique was used in all, and similar results were obtained over a range of temperatures and bath gas pressures.

Over the small temperature range covered (251–348 K) the results of Hynes *et al.*[5] could equally well be represented by either an Arrhenius expression with a small negative temature coefficient for k or by a temperature-independent rate coefficient. The results of Murrells *et al.*[6] favor the latter. For the preferred values we assume the rate coefficient to be temperature independent over the temperature range studied and take a mean of the values of Hynes *et al.*[5] and Murrells *et al.*[6] which are in good agreement with the most recent study of Diau and Lee.[1]

The main steps in the atmospheric oxidation of CS_2 initiated by HO are

$$HO + CS_2 \rightleftharpoons HOCS_2$$

$$HOCS_2 + 2O_2 \rightarrow HO_2 + SO_2 + OCS$$

Reaction of the $HOCS_2$ with O_2 predominates over reaction with NO or NO_2. Because of the nature and number of the steps involved, the overall rate of reaction of HO with CS_2 in the presence of O_2 is a complex function of both the total pressure and the pressure of O_2. Studies over a range of pressures and gas composition have established k_{eff}, the rate coefficient for HO removal in air. Hynes *et al.*[5] have obtained the following expression of k_{eff} in air at 298 K:

$$k_{eff}=\frac{1.25\times10^{-16}\exp(4550/T)}{T+1.81\times10^{-3}\exp(3400/T)}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

Studies by Murrells *et al.*[6] and Becker *et al.*[7] are in good agreement with this expression.

Despite the concordancy of such measurements of k_{eff}, significant differences are found between the values for k_{eff} based on measurements of HO removal and those based on relative rate studies of product formation. Becker *et al.*[7] have carried out both types of study in the same laboratory, employing a number of variations of the relative rate method, but the results have only confirmed the difference. The studies based on product formation give values of k_{eff} up to 50% higher than the real-time studies based on HO removal. These differences point to the need for further studies of the chemistry of the later stages of the reaction involving O_2.

Recent work by Stickel *et al.*[8] has provided some further insight into the mechanism of this complex reaction. Two types of experiment were performed. In one, the reaction was initiated by pulsed laser photolysis and product concentrations monitored in real time by tunable diode laser absorption spectroscopy. In the other, continuous photolysis was used with FTIR product detection. Products observed were OCS, SO_2, CO, and CO_2. Both experiments gave concordant values for the yields of OCS and CO of (0.83±0.08) and (0.16±0.03), respectively. The yield of CO_2 was small (<0.01). The overall yield of SO_2 (1.15±0.10) was made up of two components, a "prompt" value of (0.84±0.20) resulting from SO_2 produced in a primary channel of the reaction and a longer time component due to production of SO_2 from reaction of O_2 with SO produced in another primary channel.

The results thus suggest two primary channels, the major one leading to OCS and SO_2 and a minor channel leading to CO and SO. There are a number of possible reaction channels leading directly to these species or to their precursors which subsequently produce them on a very short time scale. The results are compatible with most of the previous product studies but some discrepancies remain, the major one being the small yield of HO found (0.05) as compared with the value of 0.3 found by Becker *et al.*[7]

References

[1] E. W- G. Diau and Y-P. Lee, J. Phys. Chem. **95**, 7726 (1991).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Inttoduction).

[4] E. R. Lovejoy, T. P. Murrells, A. R. Ravishankara, and C. J. Howard, J. Phys. Chem. **94**, 2386 (1990).

[5] A. J. Hynes, P. H. Wine, and J. M. Nicovich, J. Phys. Chem. **92**, 3846 (1988).

[6] T. P. Murrells, E. R. Lovejoy, and A. R. Ravishankara, J. Phys. Chem. **94**, 2381 (1990).

[7] K. H. Becker, W. Nelsen, Y. Su, and K. Wirtz, Chem. Phys. Lett. **168**, 559 (1990).

[8] R. E. Stickel, M. Chin, E. P. Daykin, A. J. Hynes, P. H. Wine, and T. J. Wallington, J. Phys. Chem. **97**, 13653 (1993).

HO + CH_3SH → products

No new data have been published since our last evaluation.

Preferred Values

$k = 3.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.9\times10^{-12}\exp(356/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–430 K.

Reliability

$\Delta\log k = \pm0.10$ at 298 K.

$\Delta(E/R) = \pm100$ K.

Comments on Preferred Values

The preferred values are based upon a least-squares analysis of the absolute rate coefficients of Atkinson *et al.*,[1] Wine *et al.*,[2,3] and Hynes and Wine,[4] which are in excellent agreement. The relative rate study of Barnes *et al.*[5] shows that erroneous rate coefficient data are obtained in the presence of O_2 and NO, thus accounting for the much higher value of Cox and Sheppard.[6] The preferred values are identical to our previous evaluation, IUPAC, 1992.[7]

The study of Hynes and Wine[4] shows that there is no observable effect of O_2 on the measured rate coefficient and the rate coefficients at 298 K for the reactions of the HO radical with CD_3SH[4] and CH_3SD[3] are within 15% of that for HO + CH_3SH. These data indicate[3,4] that the reaction proceeds via initial addition of HO to form the adduct $CH_3S(OH)H$.[3]

Tyndall and Ravishankara[8] have determined, by monitoring the CH_3S radical by LIF, a CH_3S radical yield from the reaction of the HO radical with CH_3SH of 1.1 ± 0.2. The reaction then proceeds by $HO + CH_3SH \rightarrow [CH_3S(OH)H] \rightarrow H_2O + CH_3S$.

References

[1] R. Atkinson, R. A. Perry, and J. N. Pitts, Jr., J. Chem. Phys. **66**, 1578 (1977).

[2] P. H. Wine, N. M. Kreutter, C. A. Gump, and A. R. Ravishankara, J. Phys. Chem. **85**, 2660 (1981).

[3] P. H. Wine, R. J. Thompson, and D. H. Semmes, Int. J. Chem. Kinet. **16**, 1623 (1984).

[4] A. J. Hynes and P. H. Wine, J. Phys. Chem. **91**, 3672 (1987).

[5] I. Barnes, V. Bastian, K. H. Becker, E. H. Fink, and W. Nelsen, J. Atmos. Chem. **4**, 445 (1986).

[6] R. A. Cox and D. Sheppard, Nature **284**, 330 (1980).

[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

[8] G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 4707 (1989).

$HO + CH_3SCH_3 \rightarrow H_2O + CH_2SCH_3$ (1)
$\rightarrow CH_3S(OH)CH_3$ (2)

$\Delta H°(1) = -107.1$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.35\times10^{-11}\exp[-(285\pm135/T)]$	297–368	Abbatt, Fenter, and Anderson, 1992[1]	(a)
$(4.98\pm0.46)\times10^{-12}$	297±2		
Branching Ratios			
$k_1/k = 0.84\pm0.15$	298	Stickel, Zhao, and Wine, 1993[2]	(b)
Reviews and Evaluations			
$k_1 = 9.6\times10^{-12}\exp(-234/T)$	250–400	IUPAC, 1992[3]	(c)
$k_2 = 1.7\times10^{-42}[O_2]\exp(7810/T)/[1+5.5\times10^{-31}[O_2]\exp(7460/T)]$	260–360		
$k_1 = 1.13\times10^{-11}\exp(-254/T)$	248–397	Atkinson, 1994[4]	(d)
$k_2 = 1.68\times10^{-42}[O_2]\exp(7812/T)/[1+5.53\times10^{-31}[O_2]\exp(7460/T)]$	~260–360		
$k_1 = 1.2\times10^{-11}\exp(-260/T)$	248–397	NASA, 1994[5]	(e)

Comments

(a) Discharge flow system with generation of HO radicals from the H + NO_2 reaction and detection by LIF. The total pressure was varied over the range 10.6–97.5 Torr of N_2. The measured rate coefficient was invariant of the total pressure over this range.

(b) For DO radical reaction with CH_3SCH_3. HDO monitored by tunable diode laser absorption spectroscopy from the DO radical reactions with CH_3SCH_3, n-hexane and cyclohexane and the branching ratio obtained by assuming (as expected) a unit HDO yield from the DO radical reactions with n-hexane and cyclohexane. The branching ratio was independent of total pressure of N_2 (10–30 Torr), temperature (298–348 K) and replacement of 10 Torr total pressure of N_2 by 10 Torr total pressure of O_2. From the temporal profiles of the HDO signals, rate coefficients k_1 for the reaction of the DO radical with CH_3SCH_3 of $(5.4\pm0.4)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 10 Torr N_2, $(5.8\pm1.9)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 30 Torr N_2, and $(4.4\pm1.0)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 348 K and 10 Torr N_2 were also obtained, in agreement with the rate coefficients for the HO radical reaction.

(c) The rate coefficient for the H-atom abstraction pathway (1) is based on the studies of Wine *et al.*[6] and Hynes *et al.*[7] and the rate coefficient for the HO addition pathway (2) utilizes the data of Hynes *et al.*[7]

(d) The rate coefficient for the abstraction process [channel (1)] was derived from the data of Wine *et al.*,[6] Hynes *et al.*,[7] Hsu *et al.*,[8] and Abbatt *et al.*[1] The rate coefficient for the addition process [channel (2)] is that of Hynes *et al.*[7]

(e) The rate coefficient for the abstraction process [channel (1)] was derived from the absolute rate coefficient data of Wine *et al.*,[6] Hynes *et al.*,[7] Hsu *et al.*,[8] and Abbatt *et al.*[1]

Preferred Values

$k = 4.8\times10^{-12}+\{(4.1\times10^{-31}\ [O_2])/(1+4.1\times10^{-20}\ [O_2]\}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 4.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 1.13\times10^{-11}\exp(-254/T)$ over the temperature range 250–400 K.

$k_2 = (4.1\times10^{-31}[O_2])/(1+4.1\times10^{-20}[O_2])$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2 = 1.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_2 = 1.7\times10^{-42}\ [O_2]\ \exp(7810/T)/\{1+5.5\times10^{-31}\ [O_2]\times\exp(7460/T)\}$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–360 K.

Reliability

$\Delta\log k=\pm0.10$ at 298 K.

$\Delta(E/R)=\pm150$ K.

$\Delta\log k_2=\pm0.3$ at 298 K and 1 bar of air.

Comments on Preferred Values

It is now recognized[4,5,7,9] that this reaction proceeds via the two reaction steps (1) and (2). The $CH_3S(OH)CH_3$ adduct radical decomposes sufficiently rapidly that in the absence of O_2 only the rate coefficient k_1 is measured. In the presence of O_2, the $CH_3S(OH)CH_3$ radical reacts by

$$CH_3S(OH)CH_3 + O_2 \rightarrow \text{products}$$

Hence only in the presence of O_2 is the addition channel (2) observed, with the observed rate constant being dependent on the O_2 concentration (but, to at least a first approximation, not on the concentration of other third bodies such as N_2, Ar or SF_6).[7]

The relative rate study of Wallington *et al.*[10] shows that previous relative rate studies were complicated by secondary reactions, and that all relative rate coefficient studies carried out in the presence of NO are of dubious quality. The most recent absolute rate coefficients measured in the absence of O_2[1,2,6–12] agree that the earliest absolute rate coefficients of Atkinson *et al.*[13] and Kurylo[14] are erroneously high, and those of Mac Leod *et al.*[15] were in error owing to heterogeneous wall reactions.[11] The preferred rate coefficient k_1 for the H-atom abstraction channel is based upon the studies of Wine *et al.*,[6] Hynes *et al.*,[7] Hsu *et al.*,[8] and Abbatt *et al.*[1] and the rate coefficient for the HO radical addition channel (step 2) utilizes the data of Hynes *et al.*[7] While the expression for k_2 is strictly valid only for 0.93 bar of air[7] (in that the rate coefficients for HO addition to CH_3SCH_3 and the reverse dissociation step may be in the fall-off regime), this equation fits well the room temperature data obtained at pressures of air from 0.07 to 0.93 bar.

References

[1] J. P. D. Abbatt, F. F. Fenter, and J. G. Anderson, J. Phys. Chem. **96**, 1780 (1992).
[2] R. E. Stickel, Z. Zhao, and P. H. Wine, Chem. Phys. Lett. **212**, 312 (1993).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[5] NASA Evaluation No. 11, 1994 (see references in Introduction).
[6] P. H. Wine, N. M. Kreutter, C. A. Gump, and A. R. Ravishankara, J. Phys. Chem. **85**, 2660 (1981).
[7] A. J. Hynes, P. H. Wine, and D. H. Semmes, J. Phys. Chem. **90**, 4148 (1986).
[8] Y.-C. Hsu, D.-S. Chen, and Y.-P. Lee, Int. J. Chem. Kinet. **19**, 1073 (1987).
[9] I. Barnes, V. Bastian, and K. H. Becker, Int. J. Chem. Kinet. **20**, 415 (1988).
[10] T. J. Wallington, R. Atkinson, E. C. Tuazon, and S. M. Aschmann, Int. J. Chem. Kinet. **18**, 837 (1986).
[11] D. Martin, J. L. Jourdain, and G. Le Bras, Int. J. Chem. Kinet. **17**, 1247 (1985).
[12] O. J. Nielsen, H. W. Sidebottom, L. Nelson, J. J. Treacy, and D. J. O'Farrell, Int. J. Chem. Kinet. **21**, 1101 (1989).
[13] R. Atkinson, R. A. Perry, and J. N. Pitts, Jr., Chem. Phys. Lett. **54**, 14 (1978).
[14] M. J. Kurylo, Chem. Phys. Lett. **58**, 233 (1978).
[15] H. Mac Leod, J. L. Jourdain, G. Poulet, and G. Le Bras, Atmos. Environ. **18**, 2621 (1984).

$HO + CH_3SSCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.2\times10^{-11}\exp[(410\pm210)/T]$	297–366	Abbatt, Fenter, and Anderson, 1992[1]	(a)
$(2.39\pm0.30)\times10^{-10}$	297		
$(2.4\pm0.9)\times10^{-10}$	298	Dominé and Ravishankara, 1992[2]	(b)
Reviews and Evaluations			
$6.0\times10^{-11}\exp(380/T)$	250–370	IUPAC, 1992[3]	(c)
$7.00\times10^{-11}\exp(350/T)$	249–367	Atkinson, 1994[4]	(d)
$6.0\times10^{-11}\exp(400/T)$	249–367	NASA, 1994[5]	(e)

Comments

(a) Discharge flow system with generation of HO radicals from the H + NO_2 reaction and detection by LIF. The total pressure was 10.5–10.9 Torr of N_2.

(b) Discharge flow system with photoionization mass spectrometric detection of CH_3SOH and CH_3S product species. The temporal profiles of these product species yielded the cited rate coefficient. The CH_3S yield from the HO radical reaction with CH_3SSCH_3 was measured to be 0.28 ± 0.20 using a pulsed laser photolysis system with LIF detection of CH_3S. The photolysis of CH_3SSCH_3 at 266 nm was used to normalize the CH_3S signal, with the CH_3S yield from the photolysis of CH_3SSCH_3 being 1.8 ± 0.2 at 248 nm.[6]

(c) The 298 K rate coefficient was the average of the absolute rate coefficients of Wine *et al.*[7] and the relative rate coefficient of Cox and Sheppard.[8]

(d) Obtained from a least-squares analysis of the absolute rate coefficients of Wine *et al.*[7] and Abbatt *et al.*[1]

(e) Based on the absolute rate coefficients of Wine *et al.*[7] and Abbatt *et al.*[1] and the room temperature relative rate coefficient of Cox and Sheppard.[8]

Preferred Values

$k = 2.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.0 \times 10^{-11} \exp(350/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Wine *et al.*,[7] Abb *et al.*,[1] and Dominé and Ravishankara[2] are in excell agreement. The preferred values are derived from a le squares analysis of the absolute rate coefficients of W *et al.*[7] and Abbatt *et al.*[1] The magnitude of the rate coe cient and the negative temperature dependence indicates th the reaction proceeds by initial HO radical addition to the atoms:

$$HO + CH_3SSCH_3 \rightarrow CH_3SS(OH)CH_3$$

References

[1] J. P. D. Abbatt, F. F. Fenter, and J. G. Anderson, J. Phys. Chem. **96**, 17 (1992).
[2] F. Dominé and A. R. Ravishankara, Int. J. Chem. Kinet. **24**, 943 (199
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[5] NASA Evaluation No. 11, 1994 (see references in Introduction).
[6] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem **97**, 5926 (1993).
[7] P. H. Wine, N. M. Kreutter, C. A. Gump, and A. R. Ravishankara, J. Ph Chem. **85**, 2660 (1981).
[8] R. A. Cox and D. W. Sheppard, Nature **284**, 330 (1980).

$HO_2 + SO_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k \leq 1 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The most recent determination[1] confirms that the reaction is slower than some earlier results[2] suggest and supports the even lower limit set by Graham *et al.*,[3] which we take as the preferred value. The preferred value is identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] J. P. Burrows, D. I. Cliff, G. W. Harris, B. A. Thrush, and J. P. T. Wilkinson, Proc. R. Soc. London Ser. A **368**, 463 (1979).
[2] W. A. Payne, L. J. Stief, and D. D. Davis, J. Am. Chem. Soc. **95**, 7614 (1973).
[3] R. A. Graham, A. M. Winer, R. Atkinson, and J. N. Pitts, Jr., J. Phys. Chem. **83**, 1563 (1979).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO_3 + H_2S \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k<1\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit to the rate coefficient is based upon the absolute rate coefficient study of Dlugokencky and Howard.[1] The preferred value is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO_3 + CS_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k<1\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based upon the absolute study of Burrows *et al.*,[1] which is consistent with the slightly higher upper limit derived by Mac Leod *et al.*[2] The preferred value is identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, J. Phys. Chem. **89**, 4848 (1985).
[2] H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO_3 + OCS \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k<1\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based upon the sole study of Mac Leod *et al.*,[1] with a somewhat higher upper limit than reported. The preferred value is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO_3 + SO_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k<1\times10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based upon the relative rate study of Daubendiek and Calvert,[1] with a much higher upper limit. This preferred upper limit to the 298 K rate coefficient is consistent with the upper limits determined in the absolute rate coefficient studies of Burrows *et al.*,[2] Wallington *et al.*,[3] Dlugokencky and Howard,[4] and Canosa-Mas *et al.*[5,6] The preferred value is identical to our previous evaluation, IUPAC, 1992.[7]

References

[1] R. L. Daubendiek and J. G. Calvert, Environ. Lett. **8**, 103 (1975).
[2] J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, J. Phys. Chem. **89**, 4848 (1985).
[3] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).
[4] E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).
[5] C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. So Faraday Trans. 2, **84**, 247 (1988).
[6] C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. So Faraday Trans. 2, **84**, 263 (1988).
[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO_3 + CH_3SH \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=9.2\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–370 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.
$\Delta(E/R)=\pm400$ K.

Comments on Preferred Values

The preferred value at 298 K is the mean of the four studies carried out to date,[1–4] which are in reasonably good agreement. Although a significant negative temperature dependence is indicated by the absolute rate coefficient study of Wallington *et al.*,[1] this is due to the rate coefficient measured at 350 K, since the rate coefficients at 280 and 298 K are identical.[1] The temperature independence determined by Dluogokencky and Howard[3] is accepted. The experimental data indicate that there is no pressure dependence of the rate coefficient, at least over the range ~0.0013–1 bar. The preferred values are identical to our previous evaluation, IUPAC, 1992.[5]

The magnitude of the rate coefficient and the lack of temperature dependence of the rate coefficient shows that this reaction proceeds by initial addition, followed by decomposition of the adduct to yield CH_3S radicals.

$$NO_3 + CH_3SH \rightleftarrows [CH_3S(ONO_2)H]^{\ddagger} \rightarrow CH_3S + HNO_3$$

This conclusion is consistent with the product studies carried out by Mac Leod *et al.*[4] and Jensen *et al.*[6] Jensen *et al.*[6] identified CH_3SO_3H (methanesulfonic acid), SO_2, HCHO, CH_3ONO_2, CH_3SNO, and HNO_3 as products of the NO_3 radical reaction with CH_3SH at 295±2 K and 740±10 Torr of purified air.

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).
[2] M. M. Rahman, E. Becker, Th. Benter, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **92**, 91 (1988).
[3] E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).
[4] H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).
[6] N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, J. Atmos. Chem. **14**, 95 (1992).

$NO_3 + CH_3SCH_3 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=1.1\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=1.9\times10^{-13}\exp(520/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–380 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.
$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The literature absolute[1–5] and relative[6] rate coefficient studies are in reasonable agreement, although the data of Wallington *et al.*[3,4] are ~20% lower than the other data. The absolute rate coefficients measured by Tyndall *et al.*,[1] Dlugokencky and Howard,[2] and Daykin and Wine[5] and the relative rate coefficient of Atkinson *et al.*[6] have been fitted to an Arrhenius expression to obtain the preferred values. The experimental data show that the rate coefficient is independent of total pressure over the range ~0.0013–1 bar. The preferred values are identical to our previous evaluation, IUPAC, 1992.[7]

The magnitude of the rate constant and the negative temperature dependence indicates that this reaction proceeds by initial addition of the NO_3 radical to the S atom. The kinetic data of Daykin and Wine[5] and Jensen *et al.*[8] for CH_3SCH_3

nd CD_3SCD_3 show that the rate determining step involves H (or D-) atom abstraction, indicating that the reaction is $NO_3 + CH_3SCH_3 \rightleftarrows [CH_3S(ONO_2)CH_3]^{\ddagger} \rightarrow CH_3SCH_2 + HNO_3$. This conclusion is consistent with the product studies of Jensen *et al.*[8,9]

References

G. S. Tyndall, J. P. Burrows, W. Schneider, and G. K. Moortgat, Chem. Phys. Lett. **130**, 463 (1986).

E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).

[3] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).

[4] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 4640 (1986).

[5] E. P. Daykin and P. H. Wine, Int. J. Chem. Kinet. **22**, 1083 (1990).

[6] R. Atkinson, J. N. Pitts, Jr., and S. M. Aschmann, J. Phys. Chem. **88**, 1584 (1984).

[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

[8] N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, J. Atmos. Chem. **14**, 95 (1992).

[9] N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, Atmos. Environ. **25A**, 1897 (1991).

$NO_3 + CH_3SSCH_3 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k = 7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 300–380 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The two absolute studies[1,2] are in reasonable agreement with respect to the room temperature rate coefficient. While the reported rate coefficient from the relative rate study[3] is an order of magnitude lower than the absolute data, the subsequent study of Atkinson *et al.*[4] shows that this is due to complexities in the experimental system used. Accordingly, the preferred values are based upon the absolute rate studies, and then mainly on the data of Dlugokencky and Howard,[2] with the error limits being sufficient to encompass the data of Wallington *et al.*[1] The preferred values are identical to our previous evaluation, IUPAC, 1992.[5]

As for the NO_3 radical reactions with CH_3SH and CH_3SCH_3, the NO_3 radical reaction with CH_3SSCH_3 is expected to proceed by initial addition, followed by decomposition of the addition adduct, possibly to yield CH_3S radicals[3]

$$NO_3 + CH_3SSCH_3 \rightleftarrows [CH_3SS(ONO_2)CH_3]^{\ddagger}$$
$$\rightarrow CH_3S + CH_3SONO_2$$

This initial reaction mechanism is consistent with the product study of Jensen *et al.*[6]

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).

[2] E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).

[3] H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).

[4] R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., J. Geophys. Res. **93**, 7125 (1988).

[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

[6] N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, J. Atmos. Chem. **14**, 95 (1992).

$HS + O_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k \leq 4 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The reaction of HS with O_2 is so slow that attempts to measure the rate coefficient have yielded only upper limits[1–5] that fall in the range 4×10^{-19} to 4×10^{-17} cm^3 molecule^{-1} s^{-1}. The preferred value is from the study of Stachnik and Molina,[4] which gives the lowest value of the limit and seems reliable, and is identical to our previous evaluation, IUPAC, 1992.[6]

References

[1] G. Black, J. Chem. Phys. **80**, 1103 (1984).

[2] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).

[3] G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **91**, 66 (1987).

[4] R. A. Stachnik and M. J. Molina, J. Phys. Chem. **91**, 4603 (1987).

[5] N. S. Wang, E. R. Lovejoy, and C. J. Howard, J. Phys. Chem. **91**, 5743 (1987).

[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HS + O_3 \rightarrow HSO + O_2$

$\Delta H° = -290$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 3.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 9.5 \times 10^{-12} \exp(-280/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–450 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

The values of k at 298 K agree reasonably well. A mean of the values from the three available studies[1-3] is taken as the preferred value. There is only one measurement of the temperature coefficient[3] which is the basis of the recommended expression, with the pre-exponential factor chosen to fit the recommended value of k at 298 K.

Since there is only one determination of the temperature dependence of k, and in view of the complexity of the secondary chemistry in these systems, substantial error limits are assigned. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).
[2] G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **91**, 66 (1987); R. N. Schindler and Th. Benter, Ber. Bunsenges. Phys. Chem. **92**, 558 (1988).
[3] N. S. Wang and C. J. Howard, J. Phys. Chem. **94**, 8787 (1990).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HS + NO + M \rightarrow HSNO + M$

$\Delta H° = -139$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 2.4 \times 10^{-31} (T/300)^{-2.5}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability
$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The pressure- and temperature-dependent measurements from Ref. 1 give a consistent picture for the association reaction and are preferred.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 2.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability
$\Delta \log k_\infty = \pm 0.5$ over the range 200–300 K.

Comments on Preferred Values

The falloff extrapolation with $F_c = 0.6$ of Ref. 1 toward k_∞ appears less certain than that to k_0. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[2]

Intermediate Falloff Range

The given k_0 and k_∞ values from Ref. 1 were based on an assumed F_c value of 0.6.

References

[1] G. Black, R. Patrick, L. E. Jusinski, and T. G. Slanger, J. Chem. Phys. **80**, 4065 (1984).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HS + NO_2 \rightarrow HSO + NO$

$\Delta H^\circ = -90$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 5.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.6 \times 10^{-11} \exp(240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–450 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

There is considerable scatter on the measured values of k with no obvious correlation with the conditions used or the technique. The presence of H atoms in the system is known to lead to complicating secondary chemistry, and some of the differences may be due to this, particularly where HS has been generated by photolysis of H_2S. In more recent studies[5,6] care has been taken to eliminate or model such effects, but significant differences persist. The preferred value at 298 K is the mean of the results of Stachnik and Molina[5] and Wang *et al.*[6] The temperature coefficient is that of Wang *et al.*[6] and the pre-exponential factor is adjusted to fit the recommended value of k at 298 K. The preferred values are identical to our previous evaluation, IUPAC, 1992.[7]

The absence of any pressure effect on the rate coefficient at pressures up to 0.96 bar[1,5] indicates that any addition channel is unimportant up to these pressures.

References

[1] G. Black, J. Chem. Phys. **80**, 1103 (1984).
[2] V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz. **3**, 1300 (1984).
[3] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).
[4] G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **91**, 66 (1987), revised by R. N. Schindler and Th. Benter, Ber. Bunsenges. Phys. Chem. **92**, 558 (1988).
[5] R. A. Stachnik and M. J. Molina, J. Phys. Chem. **91**, 4603 (1987).
[6] N. S. Wang, E. R. Lovejoy, and C. J. Howard, J. Phys. Chem. **91**, 5743 (1987).
[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HSO + O_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k \leq 2.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The reaction is slow and only an upper limit to k is available.[1]

References

[1] E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).

$$\mathrm{HSO + O_3 \rightarrow HS + 2O_2} \quad (1)$$
$$\mathrm{\rightarrow HO + SO + O_2} \quad (2)$$
$$\mathrm{\rightarrow HSO_2 + O_2} \quad (3)$$

$\Delta H°(1)=4$ kJ·mol^{-1}
$\Delta H°(2)=-94$ kJ·mol^{-1}
$\Delta H°(3)=-361$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2+k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comment
Absolute Rate Coefficients			
$k_3=2.1\times10^{-12}\exp[-(1120\pm320)/T]$	273–423	Lee, Lee, and Wang, 1994[1]	(a)
$k_3=(4.7\pm1.0)\times10^{-14}$	298		
Reviews and Evaluations			
1.1×10^{-13}	298	IUPAC, 1992[2]	(b)
1.0×10^{-13}	298	NASA, 1994[3]	(b)

Comments

(a) Discharge flow study. HSO generated by HS + O_3 reaction. Three sources of HS used (CH_3SH + O, H_2S + F, C_2H_4 + S) of which reaction of H with C_2H_4 + S was the most satisfactory. [HSO] monitored by LIF at 655 nm. [O_3] determined by light absorption at 245 nm. Channel (1) regenerates HSO by HS + O_3 → HSO + O_2; removal of HSO attributed to other channels.

(b) Based on the studies of Wang and Howard[4] and Friedl *et al.*[5]

Preferred Values

$k=1.1\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1=6\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_3=5\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.
$\Delta\log k_1=\pm0.3$ at 298 K.
$\Delta\log k_3=\pm0.3$ at 298 K.

Comments on Preferred Values

In the recent study by Lee *et al.*[1] the rate coefficient measured is that for HSO removal by all channels other than the channel giving HS as a product (channel 1) which subsequently regenerates HSO by reaction with the O_3 present. However, in our recommendations the rate coefficients measured by Lee *et al.*[1] are assigned to channel 3 on the grounds that Friedl *et al.*[5] could not detect HO production (channel 2); some further support comes from the work of Lovejoy *et al.*[6] who found that HSO_2 is readily formed by the HSO + NO_2 reaction.

The value at 298 K of k_3 found by Lee *et al.*[1] is compatible within the assigned error limits with the overall rate coefficient and the value of k_1 (7×10^{-14} cm^3 molecule^{-1} s^{-1}) found by Wang and Howard.[4]

Although Lee *et al.*[1] have measured a temperature coefficient for k_3, preferred values are only given at 298 K until further studies are made on the effects of temperature on all of the rate coefficients.

References

[1] Y.-Y. Lee, Y.-P. Lee, and N. S. Wang, J. Chem. Phys. **100**, 387 (1994).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] N. S. Wang and C. J. Howard, J. Phys. Chem. **94**, 8787 (1990).
[5] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).
[6] E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).

HSO + NO → products

No new data have been published since our last evaluation.

Preferred Values

1.0×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K.

mments on Preferred Values

The only two available measurements of $k^{1,2}$ differ by at t a factor of 26. This is unlikely to be due to the higher sures used in the Bulatov *et al.*[1] study but may arise n secondary chemistry in their HSO source, which emyed relatively large H_2S concentrations. Provisionally, the upper limit of Lovejoy *et al.*[2] is preferred. The preferred value is identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khimi. Fiz. **4**, 1353 (1985).

[2] E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

HSO + NO_2 → products

No new data have been published since our last evaluation.

Preferred Values

k 9.6×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.

iability

$\Delta\log k=\pm0.3$ at 298 K.

mments on Preferred Values

The only two measurements of $k^{1,2}$ differ by at least a ctor of 2. Lovejoy *et al.*[2] have suggested that the relatively h H_2S concentrations used by Bulatov *et al.*[1] in their work y lead to side reactions regenerating HSO. The value of ovejoy *et al.*[2] is preferred, but wide error limits are assigned awaiting confirmatory studies. The preferred value is identical to our previous evaluation, IUPAC, 1992.[3]

HO_2 was observed as a product of the reaction by Lovejoy *et al.*,[2] which they suggest arises from the sequence $HSO+NO_2 \rightarrow HSO_2 + NO$, $HSO_2 + O_2 \rightarrow HO_2 + SO_2$.

References

[1] V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz. **3**, 1300 (1984).

[2] E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

HSO_2 + O_2 → products

No new data have been published since our last evaluation.

Preferred Values

k 3.0×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K.

iability

$\Delta\log k=\pm0.8$ at 298 K.

mments on Preferred Values

There is only one study of this reaction.[1] The method used obtain the rate coefficient was indirect and this leads us to suggest substantial error limits despite the high quality of the experimental work. The preferred value is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

SO + O_2 → SO_2 + O

$\Delta H^\circ = -52.6$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=7.6\times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=1.6\times 10^{-13}$ exp($-2280/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 230–420 K.

Reliability
$\Delta\log k=\pm 0.15$ at 298 K.
$\Delta(E/R)=\pm 500$ K.

Comments on Preferred Values

This reaction is very slow and measurement of k is subject to error due to impurities. For this reason, Black *et al.*[1,2] favor their lower values of k at 298 K obtained in the temperature dependence study.[2] The Goede and Schurath[3] values are systematically lower than those from Ref. 2 by about 35%, but appear to have less experimental uncertainty at temperatures <300 K. The preferred value for k at 298 K and for E/R are mean values from Refs. 2 and 3. The A factor is adjusted to give the preferred value at 298 K. The preferred values differ slightly from those in our previous evaluation, IUPAC, 1992.[4]

[1] G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).
[2] G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **93**, 598 (1982).
[3] H.-J. Goede and U. Schurath, Bull. Soc. Chim. Belg. **92**, 661 (1983).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$SO + O_3 \rightarrow SO_2 + O_2$

$\Delta H°=-444.5$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=8.9\times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=4.5\times 10^{-12}$ exp($-1170/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 230–420 K.

Reliability
$\Delta\log k=\pm 0.10$ at 298 K.
$\Delta(E/R)=\pm 150$ K.

Comments on Preferred Values

The data of Black *et al.*[1,2] are in good agreement with earlier work.[3,4] The preferred value at 298 K is the simple mean of measurements from Refs. 1–4. The temperature dependence from Black *et al.*[2] is accepted since this study covered a much larger temperature range than the earlier work,[3] which nevertheless gave a value of E/R within the experimental error of the later study.[2] The preferred values are identical to our previous evaluation, IUPAC, 1992.[5]

References

[1] G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).
[2] G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **93**, 598 (1982).
[3] C. J. Halstead and B. A. Thrush, Proc. R. Soc. London Ser. A **295**, 380 (1966).
[4] J. S. Robertshaw and I. W. M. Smith, Int. J. Chem. Kinet. **12**, 729 (1980).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$SO + NO_2 \rightarrow SO_2 + NO$

$\Delta H°=-244.8$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=1.4\times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 210–360 K.

Reliability
$\Delta\log k=\pm 0.1$ at 298 K.
$\Delta(E/R)=\pm 100$ K.

Comments on Preferred Values

The measurements of Brunning and Stief[1] are the only data available on the temperature dependence of k and indicate no measurable change in k over the range 210–363 K. This finding is the basis for our present recommendation for the temperature coefficient. All of the studies[1–4] of k at 298 K are in good agreement and a mean of them all is taken for our recommended value. The preferred values are identical to our previous evaluation, IUPAC, 1992.[5]

References

[1] J. Brunning and L. J. Stief, J. Chem. Phys. **84**, 4371 (1986).

[2] G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).

[3] M. A. A. Clyne, C. J. Halstead, and B. A. Thrush, Proc. R. Soc. London, Ser. A **295**, 355 (1966).

[4] M. A. A. Clyne and A. J. MacRobert, Int. J. Chem. Kinet. **12**, 79 (1980).

[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$SO_3 + H_2O \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k < 6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

It was suspected that wall effects were significant in the flow system of Castleman *et al.*[1] and this was confirmed by Wang *et al.*[2] who were able to reduce wall effects by appropriate wall coatings. The upper limit of Wang *et al.*[2] is accepted as our preferred value, which is identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] A. W. Castleman, Jr., R. E. Davis, H. R. Munkelwitz, I. N. Tang, and W. P. Wood, Int. J. Chem. Kinet., Symp. **1**, 629 (1975).

[2] X. Wang, Y. G. Yin, M. Suto, L. C. Lee, and H. E. O'Neal, J. Chem. Phys. **89**, 4853 (1988).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$SO_3 + NH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.9 \pm 1.5) \times 10^{-11}$	298	Shen, Suto, and Lee, 1990[1]	(a)
Reviews and Evaluations			
6.9×10^{-11}	298	NASA, 1994[2]	(b)

Comments

(a) Flow system with NH_3 in large excess. [SO_3] monitored by observation of SO_2 fluorescence in range 280–390 nm from photofragmentation of SO_3 by 147 nm radiation. He carrier gas (1–2 Torr).

(b) Accepted the value of Shen *et al.*[1]

Preferred Values

$k = 6.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only available data is from the work of Shen *et al.*[1] Their value of k is accepted with substantial error limits until confirmatory studies are made.

References

[1] G. Shen, M. Suto, and L. C. Lee, J. Geophys. Res. **95**, 13981 (1990).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CS + O_2 \rightarrow CO + SO$ (1)
$\rightarrow OCS + O$ (2)

$\Delta H^\circ(1) = -378$ kJ·mol^{-1}
$\Delta H^\circ(2) = -165$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 2.9 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.6$ at 298 K.

Comments on Preferred Values

The reaction of CS with O_2 is slow at 298 K and difficult to study. In the reported studies[1–7] the technique used by Black *et al.*[4] seems the most suitable for avoiding difficulties associated with the slowness of the reaction and their value at 298 K is preferred.

The relative importance of the two possible reaction channels is in dispute. Evidence from the photochemical and explosion limit studies[5–7] indicate comparable importance but in a more direct flow system study[3] k_1 was found to be at least an order of magnitude less than k_2. However, the absolute value of k_2 obtained in the fast flow study[3] appears to be unacceptably high. We make no recommendation for the branching ratio.

The one available measurement of k at higher temperatures,[3] when combined with the 298 K values leads to an Arrhenius expression with an extremely low pre-exponential factor. No recommendation is made for the temperature dependence. The preferred value is identical to our previous evaluation, IUPAC, 1992.[8]

References

[1] A. B. Callear and D. R. Dickson, reported in G. Hancock and I. W. M. Smith, Trans. Faraday Soc. **67**, 2586 (1971).
[2] W. H. Breckenridge, W. S. Kolln, and D. S. Moore, Chem. Phys. Lett. **32**, 290 (1975).
[3] R. J. Richardson, J. Phys. Chem. **79**, 1153 (1975).
[4] G. Black, L. E. Jusinski, and T. G. Slanger, Chem. Phys. Lett. **102**, 64 (1983).
[5] W. P. Wood and J. Heicklen, J. Phys. Chem. **75**, 854 (1971).
[6] W. P. Wood and J. Heicklen, J. Photochem. **2**, 173 (1973/74).
[7] W. P. Wood and J. Heicklen, J. Phys. Chem. **75**, 861 (1971).
[8] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CS + O_3 \rightarrow OCS + O_2$

$\Delta H^\circ(1) = -556.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 3.0 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The only available measurement of k is that of Black *et al.*[1] Their value is accepted, but substantial error limits are assigned. The preferred value is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] G. Black, L. E. Jusinski, and T. G. Slanger, Chem. Phys. Lett. **102**, 64 (1983).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CS + NO_2 \rightarrow OCS + NO$

$\Delta H^\circ(1) = -357$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 7.6\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The only available measurement of k is that of Black *et al.*[1] Their value is accepted, but substantial error limits are assigned. The preferred value is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] G. Black, L. E. Jusinski, and T. G. Slanger, Chem. Phys. Lett. **102**, 64 (1983).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_2SH + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.5\pm1.0)\times10^{-12}$	298	Anastasi *et al.*, 1992[1]	(a)
$(4.6\pm1.9)\times10^{-12}$	298	Rahman *et al.*, 1992[2]	(b)
Reviews and Evaluations			
6.5×10^{-12}	298	NASA, 1994[3]	(c)

Comments

(a) Pulse radiolysis of CH_3SH-O_2-SF_6 mixtures at 1 bar total pressure. CH_2SH and CH_3S radicals were generated by reactions of the radiolytically produced F atoms with CH_3SH. $[CH_2SH]$ was monitored by UV absorption over range 220–380 nm.

(b) Fast flow discharge study. CH_2SH radicals were generated by reaction of F atoms with CH_3SH. $[CH_2SH]$ was monitored by mass spectrometry. Source reactions were simulated to check consumption of F atoms. Total pressure 3 mbar.

(c) Mean of the rate coefficients of Anastasi *et al.*[1] and Rahman *et al.*[2]

Preferred Values

$k = 6.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only two measurements of k differ by almost a factor of 2. The values of $k(CH_2SH + NO_2)$ measured in these two studies also differ, although the error limits are large enough to encompass the two results. Until further studies are carried out, a mean of the two values is recommended with substantial error limits.

References

[1] C. Anastasi, M. Broomfield, O. J. Nielsen, and P. Pagsberg, J. Phys. Chem. **96**, 696 (1992).

[2] M. M. Rahman, E. Becker, U. Wille, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **96**, 783 (1992).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CH_2SH + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5\pm1.2)\times10^{-11}$	298	Rahman *et al.*, 1992[1]	(a)
Reviews and Evaluations			
3.5×10^{-11}	298	NASA, 1994[2]	(b)

Comments

(a) Fast-flow discharge study. CH_2SH radicals were generated by the reaction of F atoms with CH_3SH, and monitored by MS. Source reactions were simulated to check consumption of F atoms. Total pressure 3 mbar.
(b) Accepted the rate coefficient of Rahman *et al.*[1]

Preferred Values

$k = 3.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only available determination of k^1 is accepted, but with substantial error limits until confirmatory studies can be made.

References

[1] M. M. Rahman, E. Becker, U. Wille, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **96**, 783 (1992).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CH_2SH + NO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.2) \times 10^{-11}$	298	Anastasi *et al.*, 1992[1]	(a)
Reviews and Evaluations			
1.9×10^{-11}	298	NASA, 1994[2]	(b)

Comments

(a) Pulse radiolysis of CH_3SH-O_2-SF_6 mixtures at 1 bar total pressure. CH_2SH and CH_3S radicals were generated by reactions of the radiolytically produced F atoms with CH_3SH. $[CH_2SH]$ was monitored by UV absorption over the wavelength range 220–380 nm.
(b) Based on the rate coefficient of Anastasi *et al.*[1]

Preferred Values

$k = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only available determination of k^1 is accepted, but with substantial error limits until confirmatory studies are made.

References

[1] C. Anastasi, M. Broomfield, O. J. Nielsen, and P. Pagsberg, J. Phys. Chem. **96**, 696 (1992).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CH_2SH + NO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.8 \pm 1.0) \times 10^{-11}$	298	Anastasi *et al.*, 1992[1]	(a)
$(6.9 \pm 4) \times 10^{-11}$	298	Rahman *et al.*, 1992[2]	(b)
Reviews and Evaluations			
5.2×10^{-11}	298	NASA, 1994[3]	(c)

Comments

(a) Pulse radiolysis of CH_3SH-O_2-SF_6 mixtures at 1 bar total pressure. CH_2SH and CH_3S radicals were generated by reactions of the radiolytically produced F atoms with CH_3SH. [CH_2SH] was monitored by UV absorption over the wavelength range 220–380 nm.

(b) Fast flow discharge study. CH_2SH radicals were generated by the reaction of F atoms with CH_3SH and were monitored by MS. Source reactions were simulated to check consumption of F atoms. Total pressure 3 mbar.

(c) Average of the rate coefficients of Anastasi *et al.*[1] and Rahman *et al.*[2]

Preferred Values

$k = 4.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The only two measurements of $k^{1,2}$ differ substantially but because the error limits are large enough to encompass the two results it is difficult to know whether the difference is significant. In the same two studies the values obtained for $k(CH_2SH + O_2)$ differed to the same degree with much smaller error limits.

Until further studies are carried out, we recommend a weighted mean of the two values and substantial error limits.

References

[1] C. Anastasi, M. Broomfield, O. J. Nielsen, and P. Pagsberg, J. Phys. Chem. **96**, 696 (1992).

[2] M. M. Rahman, E. Becker, U. Wille, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **96**, 783 (1992).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CH_3S + O_2 + M \rightarrow CH_3SOO + M$

$\Delta H = -49$ kJ·mol^{-1}

Rate coefficient data

cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
$(1.81 \pm 0.28) \times 10^{-13}$ (80 Torr He)	216	Turnipseed, Barone, and Ravishankara, 1992[1]	(a)
$(1.55 \pm 0.23) \times 10^{-13}$ (80 Torr He)	222		
$(1.05 \pm 0.20) \times 10^{-13}$ (80 Torr He)	233		
$(9.0 \pm 1.6) \times 10^{-14}$ (80 Torr He)	237		
$(5.62 \pm 0.84) \times 10^{-14}$ (80 Torr He)	242		
$(7.0 \pm 2.0) \times 10^{-14}$ (80 Torr He)	250		

Comments

(a) Pulsed laser photolysis system with LIF detection of CH_3S radicals. The measured rate coefficients were observed to vary with the total pressure and the diluent gas. An upper limit to the rate coefficient for the reaction of the CH_3SOO radical with O_2 of 4×10^{-17} cm^3 molecule^{-1} s^{-1} at 258 K was also derived. The CH_3S-OO bond energy was determined to be 49 kJ mol^{-1} at 298 K from measurements of the equilibrium constant over the temperature range 216–258 K, with $\Delta H_f(CH_3SOO) = 75.7 \pm 4.2$ kJ mol^{-1} at 298 K.[1]

Preferred Values

See Table.

Reliability

$\Delta \log k = \pm 0.3$ over the temperature range 216–250 K at 80 Torr He.

Comments on Preferred Values

The study of Turnipseed *et al.*[1] is the first to observe addition of O_2 to the CH_3S radical to form CH_3SOO [and not $CH_3S(O)O$] because the reaction was observed to be reversible leading to equilibrium between CH_3S radicals, O_2 and CH_3SOO radicals.[1] Previous studies of the reaction of CH_3S radicals with O_2 at 298 K[2–4] did not observe the equilibrium addition of O_2 to CH_3S radicals, and the rate coefficients measured[2–5] correspond to upper limits to the rate coefficients for the reactions

$$CH_3S + O_2 \rightarrow \text{products other than } CH_3SOO$$

and/or

$$CH_3SOO + O_2 \rightarrow \text{products.}$$

The reaction of CH_3S radicals with O_2 to form the CH_3SOO radical, and the reverse reaction, result in ~33% of CH_3S radicals being present as the CH_3SOO adduct at 298 K and ground level,[1] with the [CH_3SOO]/[CH_3S] ratio being strongly temperature dependent.[1]

References

[1] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **96**, 7502 (1992).

[2] R. J. Balla, H. H. Nelson, and J. R. McDonald, J. Chem. Phys. **109**, 101 (1986).

[3] G. Black and L. E. Jusinski, J. Chem. Soc. Faraday Trans. 2, **86**, [illegible] (1986).

[4] G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 2426 (19[illegible]

[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_3SOO + M \rightarrow CH_3S + O_2 + M$

$\Delta H° = 49$ kJ·mol^{-1}

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Comments
$(1.99 \pm 0.74) \times 10^3$ (80 Torr He)	216	Turnipseed, Barone, and Ravishankara, 1992[1]	(a)
$(3.20 \pm 0.80) \times 10^3$ (80 Torr He)	222		
$(9.1 \pm 2.6) \times 10^3$ (80 Torr He)	233		
$(1.00 \pm 0.12) \times 10^4$ (80 Torr He)	237		
$(1.28 \pm 0.12) \times 10^4$ (80 Torr He)	242		
$(2.4 \pm 0.4) \times 10^4$ (80 Torr He)	250		
$> 3.5 \times 10^4$ (80 Torr He)	258		

Comments

(a) Pulsed laser photolysis system with LIF detection of CH_3S radicals. The formation and decay rate coefficients of CH_3SOO radicals were derived from the observed time-concentration profiles of CH_3S radicals in the presence of O_2. The measured rate coefficients for the reactions $CH_3S + O_2 \rightleftarrows CH_3SOO$ were observed to vary with total pressure and with the diluent gas.

Preferred Values

See Table.

Reliability

$\Delta \log k = \pm 0.3$ at 80 Torr He over the temperature range 216–250 K.

Comments on Preferred Values

The data presented by Turnipseed *et al.*[1] are the first reported for the dissociation of the CH_3SOO radical (see also the data sheet in this evaluation for the reverse reaction $CH_3S + O_2 + M \rightarrow CH_3SOO + M$). In the atmosphere, ~33% of CH_3S radicals will be present as the CH_3SOO adduct at 298 K and ground level,[1] with the $[CH_3SOO]/[CH_3S]$ ratio being strongly temperature dependent.[1]

References

[1] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **96**, 7502 (1992).

$CH_3S + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.7 \pm 1.4) \times 10^{-12}$	300	Dominé, Ravishankara, and Howard, 1992[1]	(a)
$1.98 \times 10^{-12} \exp[(290 \pm 40)/T]$	295–359	Turnipseed, Barone, and Ravishankara, 1993[2]	(b)
5.16×10^{-12}	298		
Reviews and Evaluations			
5.4×10^{-12}	298	Tyndall and Ravishankara, 1991[3]	(c)
4.1×10^{-12}	298	IUPAC, 1992[4]	(d)
$2.0 \times 10^{-12} \exp(290/T)$	295–359	NASA, 1994[5]	(e)

Comments

(a) Discharge flow study. CH_3S radicals were generated by reaction of Cl with CH_3SH or O with CH_3SSCH_3. Photoionization mass spectrometry was used to monitor CH_3, CH_3S, CH_3SO, CH_2S, CH_3SS, CH_3SSO, CH_2SO, C_2H_5. C_2F_3Cl was added to scavenge OH radicals and hence suppress OH radical-initiated chain reaction which regenerates CH_3S. Some curvature was observed on $[CH_3S]$ logarithmic decay plots in excess O_3. The initial slope was used to calculate k.

(b) Pulsed laser photolysis of $(CH_3)_2S$-O_3 (193 nm) or $(CH_3)_2S_2$-O_3 (248 nm) mixtures in bath gas of He, N_2, or SF_6. $[CH_3S]$ was monitored by LIF. Pressure range 20–200 Torr. No evidence for chain reaction was observed under the experimental conditions employed for the rate coefficient determinations.

(c) Based on the work of Tyndall and Ravishankara[6] and Dominé *et al.*[1] The corrections made in the work of Tyndall and Ravishankara[6] to convert the measured value of k (5.1×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) to the quoted value (4.1×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) is now known to be unjustified.

(d) Accepted the value of Tyndall and Ravishankara.[6]

(e) Derived from the absolute rate coefficients of Tyndall and Ravishankara,[6] Dominé *et al.*,[1] and Turnipseed *et al.*[2]

Preferred Values

$k=5.4\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$k=2.0\times10^{-12}\exp(290/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 290–360 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

It is difficult to study this reaction because in some conditions rapid chain processes involving the reaction products occur to regenerate CH_3S radicals. This complication appears to be absent in the most recent study by Turnipseed *et al.*[2] Their value of k at 298 K is in good agreement with other studies in which care was taken to allow for this complication.[1,6] The mean of the values from the two most recent studies[1,2] is taken as our recommended value at 298 K.

There is only one study of the temperature dependence of k.[2] Its findings are accepted with substantial error limits and the pre-exponential factor is adjusted to yield the recommended value of k at 298 K.

References

[1] F. Dominé, A. R. Ravishankara, and C. J. Howard, J. Phys. Chem. **96**, 2171 (1992).

[2] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).

[3] G. S. Tyndall and A. R. Ravishankara, Int. J. Chem. Kinet. **23**, 483 (1991).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

[6] G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 4707 (1989).

$CH_3S + NO + M \rightarrow CH_3SNO + M$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0=3.2\times10^{-29}\,(T/300)^{-4}\,[N_2]$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 250–450 K.

Reliability

$\Delta\log k_0=0.3$ at 298 K.

$\Delta n=\pm2$.

Comments on Preferred Values

The preferred values are based on the data of Balla *et al.*[1] Although the falloff extrapolations in Ref. 1 were made with a theoretically improbable temperature coefficient of F_c, the low-pressure rate coefficients are much less influenced by this extrapolation than the high-pressure rate coefficients.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty=4\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, independent of temperature over the range 250–450 K.

Reliability

$\Delta\log k_\infty=\pm0.5$ over the temperature range 250–450 K.

Comments on Preferred Values

The negative temperature coefficient of k_∞ reported in Ref. 1 is most probably due to an increasing underestimate of the falloff corrections with increasing temperature. We recommend the use of the extrapolated k_∞ value at 298 K over large temperature ranges together with $F_c = \exp(-T/580)$. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.[3]

Intermediate falloff range

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	P/Torr	M	Temp./K	Reference	Comments
Relative Rate Coefficients					
$(1.69\pm0.04)\times10^{-11}$	21	He	227	Turnipseed, Barone, and Ravishankara, 1993[2]	(a)
$(1.30\pm0.09)\times10^{-11}$	19	He	242		
$(1.89\pm0.08)\times10^{-11}$	19	He	242		

Comments

(a) CH_3S radicals were generated by either photolysis of dimethyl sulfide at 193 nm or photolysis of dimethyl disulfide at 248 nm. The decay of CH_3S radical concentrations was followed by LIF. Experiments were performed under slow gas flow conditions.

References

[1] R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **109**, 101 (1986)

[2] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_3S + NO_2 \rightarrow CH_3SO + NO$

$\Delta H° = -135$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.1\times10^{-11}\exp[(320\pm40)/T]$	242–350	Turnipseed, Barone, and Ravishankara, 1993[1]	(a)
6.3×10^{-11}	298		
Reviews and Evaluations			
5.5×10^{-11}	298	Tyndall and Ravishankara, 1991[2]	(b)
5.6×10^{-11}	298	IUPAC, 1992[3]	(b)
$2.1\times10^{-11}\exp(320/T)$	242–350	NASA, 1994[4]	(c)

Comments

(a) Pulsed laser photolysis at 193 nm or 248 nm of $(CH_3)_2S$-NO_2 or $(CH_3)_2S_2$-NO_2 mixtures respectively in bath gas of He, N_2 or SF_6. $[CH_3S]$ was monitored by LIF. No effect of pressure on k was observed (20–200 Torr of He).

(b) Based on the results of Tyndall and Ravishankara[5] and of Dominé *et al.*[6]

(c) Based on the rate coefficients of Tyndall and Ravishankara[5] and Turnipseed *et al.*[1]

Preferred Values

$k = 5.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.0\times10^{-11}\exp(320/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–350 K.

Reliability

$\Delta\log k = \pm0.15$ at 298 K.

$\Delta(E/R) = \pm300$ K.

Comments on Preferred Values

The recommended value at 298 K is the mean of the three most recent studies,[1,5,6] which are in good agreement.

There are two studies[1,7] of the temperature dependence of k, both giving a positive value of E/R but differing significantly in magnitude. Balla *et al.*[7] obtain a very small value of E/R but obtain values of k nearly twice as large as those found in the other studies. It has been suggested[5] that this could arise from secondary chemistry arising from the higher radical concentrations used in the work of Balla *et al.*[7] The alternative value of Turnipseed *et al.*[1] is preferred but substantial error limits are recommended. The preexponential factor in the expression for k is based on the value of E/R from Turnipseed *et al.*[1] and the recommended value of k at 298 K.

The lack of pressure dependence of k found in the recent[1] and earlier studies[5,7] is consistent with the main pathway for the reaction proceeding directly to NO and CH_3SO rather than by addition to give CH_3SNO_2. Product studies[5,8] are in agreement with this conclusion.

References

[1] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).

[2] G. S. Tyndall and A. R. Ravishankara, Int. J. Chem. Kinet. **23**, 483 (1991).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

[5] G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 2426 (1989).

[6] F. Dominé, T. P. Murrells, and C. J. Howard, J. Phys. Chem. **94**, 5839 (1990).

[7] R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **109**, 101 (1986).

[8] I. Barnes, V. Bastian, K. H. Becker, and H. Niki, Chem. Phys. Lett. **140**, 451 (1987).

$CH_3SO + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.0\pm3.0)\times10^{-13}$	300	Dominé, Ravishankara, and Howard, 1992[1]	(a)
Reviews and Evaluations			
1×10^{-12}	298	IUPAC, 1992[2]	(b)
6.0×10^{-13}	298	NASA, 1994[3]	(c)

Comments

(a) Discharge flow study. CH_3S radicals were generated by reaction of Cl with CH_3SH. Photoionization mass spectrometry was used to monitor [CH_3SO] and [CH_3S] in CH_3S-O_3 system. CH_3SO radicals were produced by $CH_3S + O_3 \rightarrow CH_3SO + O_2$ in 15% yield, independent of pressure in the range 0.7–2.2 Torr He. Reaction of O with $C_2H_5SCH_3$ was used as a source of CH_3SO to measure $k(CH_3SO + O_3)$. Value considered preliminary.

(b) Accepted the value of Tyndall and Ravishankara.[4]

(c) Based on the rate coefficient of Dominé *et al.*,[1] which is in agreement with the less direct study of Tyndall and Ravishankara.[4]

Preferred Values

$k=6.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

Comments on Preferred Values

The measurement of k by Dominé *et al.*[1] is more direct than the previous study of Tyndall and Ravishankara[4] in which the result was derived by a complex analysis of the reaction system. However, there are still a number of uncertainties in the study by Dominé *et al.*,[1] who consider their quoted value of k to be preliminary. This value[1] is accepted but substantial error limits are recommended.

References

[1] F. Dominé, A. R. Ravishankara, and C. J. Howard, J. Phys. Chem. **96**, 2171 (1992).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 4707 (1989).

$CH_3SO + NO_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=1.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.5$ at 298 K.

Comments on Preferred Values

The measured values[1–3] of k at 298 K agree within their error limits, some of which are substantial. The preferred value is that of Dominé *et al.*,[3] which lies between the other two values both of which have much larger error limits. This rate coefficient is difficult to measure because of the lack of a clean primary source of CH_3SO radicals and the complexity of the secondary chemistry; substantial error limits are suggested. The preferred value is identical to that in our previous evaluation IUPAC, 1992.[4]

References

[1] A. Mellouki, J. L. Jourdain, and G. Le Bras, Chem. Phys. Lett. **148**. (1988).

[2] G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 2426 (198

[3] F. Dominé, T. P. Murrells, and C. J. Howard, J. Phys. Chem. **94**, 58 (1990).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_3SOO + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<8\times10^{-13}$	228	Turnipseed, Barone, and Ravishankara, 1993[1]	(a)
Reviews and Evaluations			
$<8.0\times10^{-13}$	227	NASA, 1994[2]	(b)

Comments

(a) Pulsed laser photolysis of $(CH_3)_2S$-O_2-O_3 mixtures at 193 nm in bath gas of He, N_2, or SF_6. $CH_3S + O_2 \rightleftharpoons CH_3SO_2$ equilibrium established. $[CH_3S]$ was monitored by LIF. $[CH_3S]$ temporal profiles were simulated to obtain k. $k(CH_3S + O_3)$ obtained in the same study was used in the fitting procedure.

(b) Based on the upper limit to the rate coefficient obtained by Turnipseed *et al.*[1]

Preferred Values

$k<8\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 228 K.

Comments on Preferred Values

The single study of the rate of this reaction[1] has provided only an upper limit to k at 228 K, which is accepted as the preferred value.

References

[1] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CH_3SOO + NO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.10\pm0.38)\times10^{-11}$	227–255	Turnipseed, Barone, and Ravishankara, 1993[1]	(a)
Reviews and Evaluations			
1.1×10^{-11}	227–256	NASA, 1994[2]	(b)

Comments

(a) Pulsed laser photolysis of $(CH_3)_2S_2$-O_2-NO mixtures at 248 nm with He or SF_6 as the bath gas. Only a limited pressure range could be studied (16–21 Torr He, 19 Torr SF_6), but no effect of pressure on k was observed. $[CH_3S]$ was monitored by LIF and the temporal profile simulated to obtain k.

(b) Based on the sole study of Turnipseed *et al.*[1]

Preferred Values

$k=1.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 227–255 K.

Reliability

$\Delta\log k=\pm0.3$ over the range 227–255 K.

Comments on Preferred Values

The value of k obtained in the only study of this reaction[1] is accepted but substantial error limits are assigned until confirmatory studies are made.

References

[1] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CH_3SOO + NO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.2\pm0.6)\times10^{-11}$	227–246	Turnipseed, Barone, and Ravishankara, 1993[1]	(a)
Reviews and Evaluations			
2.2×10^{-11}	227–246	NASA, 1994[2]	(b)

Comments

(a) Pulsed laser photolysis of $(CH_3)_2S_2$-O_2-NO_2 mixtures at 248 nm in He (80–350 Torr) or SF_6 (65 Torr). [CH_3S] was monitored and the temporal profile simulated to obtain k. No variation of k with pressure or temperature was found.

(b) Based on the sole study of Turnipseed *et al.*[1]

Preferred Values

$k=2.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 227–246 K.

Reliability

$\Delta\log k=\pm0.3$ over the range 227–246 K.

Comments on Preferred Values

The value of k obtained in the only study[1] of this reaction is accepted but substantial error limits are assigned until confirmatory studies are made.

References

[1] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CH_3SCH_2 + O_2 \rightarrow CH_3SCH_2O_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.7\pm0.4)\times10^{-12}$ (1 bar)	298	Wallington, Ellermann, and Nielsen, 1993[1]	(a)
2.3×10^{-13} (1 Torr He)	298	Butkovskaya and Le Bras, 1994[2]	(b)
1.9×10^{-13} (1 Torr He)	298		

Comments

(a) Pulse radiolysis of SF_6-CH_3SCH_3-O_2 mixtures. CH_3SCH_2 radicals were generated by reaction of F atoms with CH_3SCH_3, and monitored in absorption at 290 nm. The total pressure was approximately 1 bar.

(b) Discharge flow study of the NO_3-CH_3SCH_3-Br_2-O_2 system at 1 Torr He. NO_3 radicals were produced by F + HNO_3 reaction added to CH_3SCH_3 to give CH_3SCH_2. Subsequent addition of Br_2-O_2 mixtures allowed monitoring of competition between O_2 and Br_2 for CH_3SCH_2. Competition followed by mass spectrometric measurement of [CH_3SCH_2Br] profile. Modeling of profile gave $k=2.3\times10^{-13}$ cm^3 molecule^{-1} s^{-1}. Similar study of Cl-Cl_2-CH_3SCH_3-O_2 system in which CH_3SCH_2 was produced by Cl + CH_3SCH_3 reaction gave $k=1.9\times10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k=5.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.

Reliability

$\Delta\log k=\pm0.4$ at 298 K and 1 bar.

Comments on Preferred Values

The preferred value of k is taken from the study of Wallington *et al.*[1] Until confirmatory studies are made we confine our recommendations to 1 bar and assign substantial error limits.

References

[1] T. J. Wallington, T. Ellermann, and O. J. Nielsen, J. Phys. Chem. **97**, 8442 (1993).

[2] N. I. Butkovskaya and G. Le Bras, J. Phys. Chem. **98**, 2582 (1994).

$CH_3SCH_2O_2 + NO \rightarrow CH_3SCH_2O + NO_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.9\pm0.6)\times10^{-11}$	298	Wallington, Ellermann, and Nielsen, 1993[1]	(a)
Reviews and Evaluations			
1.9×10^{-11}	298	NASA, 1994[2]	(b)

Comments

(a) Pulse radiolysis of CH_3SCH_3-SF_6-O_2-NO mixtures. Generation of $CH_3SCH_2O_2$ radicals occurred by F + $CH_3SCH_3 \rightarrow CH_3SCH_2$ + HF, followed by $CH_3SCH_2 + O_2 \rightarrow CH_3SCH_2O_2$. [$NO_2$] was monitored at 400 nm. Yield of NO_2 compared with yield of F atoms suggest that 80% of the reaction leads to NO_2 production.

(b) Based on the rate coefficient of Wallington *et al.*[1]

Preferred Values

$k=1.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.4$ at 298 K.

Comments on Preferred Values

The preferred value of k is taken from the only study of this reaction.[1] Substantial error limits are assigned until confirmatory studies are made.

References

[1] T. J. Wallington, T. Ellermann, and O. J. Nielsen, J. Phys. Chem. **97**, 8442 (1993).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CH_3SCH_2O_2 + CH_3SCH_2O_2 \rightarrow CH_3SCH_2OH + CH_3SCHO + O_2$ (1)
$\rightarrow 2CH_3SCH_2O + O_2$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq7.9\times10^{-12}$	298	Wallington, Ellermann, and Nielsen, 1993[1]	(a,b)

Comments

(a) k is defined by $-d[CH_3SCH_2O_2]/dt=2k[CH_3SCH_2O_2]^2$ and has been derived from the measured overall second-order decay of $CH_3SCH_2O_2$ radicals (k_{obs}).

(b) Pulse radiolysis study of CH_3SCH_3-O_2-SF_6 mixtures with monitoring of $CH_3SCH_2O_2$ radical concentrations by UV absorption with $\sigma_{250}=(4.3\pm0.7)\times10^{-18}$ cm^2 molecule^{-1}. The observed value of $k_{obs}=(7.9\pm1.4)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} is an upper limit to k because of the possibility of secondary reactions giving rise to an increasing decay rate of $CH_3SCH_2O_2$ radicals (see Comments on Preferred Values).

Preferred Values

$k \leq 8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

We have recommended an upper limit to the overall rate coefficient at 298 K, as determined by Wallington *et al.*[1] There is no information as yet on the products of the self-reactions of the $CH_3SCH_2O_2$ radicals, although it has been suggested that the alkoxy radical, CH_3SCH_2O, could react as follows: $CH_3SCH_2O \rightarrow CH_3S + HCHO$ and that the CH_3S radicals could react with the $CH_3SCH_2O_2$ radicals, leading to an enhanced decay rate of these radicals.

References

[1] T. J. Wallington, T. Ellermann, and O. J. Nielsen, J. Phys. Chem. **97**, 8442 (1993).

$CH_3SS + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.6\pm1.1)\times10^{-13}$	300	Dominé, Ravishankara, and Howard, 1992[1]	(a)
Reviews and Evaluations			
4.6×10^{-13}	298	NASA, 1994[2]	(b)

Comments

(a) Discharge-flow study. Photoionization mass spectrometry was used to monitor [CH_3], [CH_3S], [CH_3SO], [CH_2S], [CH_3SS], [CH_3SSO], [CH_2SO], and [C_2H_5] produced in reactions of O_3 with CH_3S and CH_3SO. CH_3S radicals were generated by Cl + CH_3SH or O + $(CH_3)_2S_2$ reactions. CH_3SS was observed to be formed in the CH_3S source and thought to be due to the $CH_3S + S_2$ reaction on walls. [CH_3SS] was monitored in the presence of excess O_3 to obtain k.

(b) Accepted the value of Dominé *et al.*[1]

Preferred Values

$k=4.6\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

Comments on Preferred Values

The only available measurement of k^1 is accepted but substantial error limits are assigned until confirmatory studies are made.

References

[1] F. Dominé, A. R. Ravishankara, and C. J. Howard, J. Phys. Chem. **96**, 2171 (1992).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CH_3SS + NO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.8\pm0.3)\times10^{-11}$	297	Dominé, Murrells, and Howard, 1990[1]	(a)
Reviews and Evaluations			
1.8×10^{-11}	298	NASA, 1994[2]	(b)

Comments

(a) Fast-flow discharge study. CH_3SS radicals were produced as a by-product of CH_3S radical production. CH_3S radicals were mainly produced by Cl + CH_3SH reaction but other sources of CH_3S, e.g., O + $(CH_3)_2S_2$ reaction, also produce CH_3SS. $[CH_3SS]$ was monitored by photoionization mass spectrometry in excess NO_2.

(b) Accepted the value of Dominé *et al.*[1]

Preferred Values

$k = 1.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The study of Dominé *et al.*[1] has provided the only available value for the rate coefficient of this reaction. This value is accepted but with substantial error limits until confirmatory studies are made.

References

[1] F. Dominé, T. P. Murrells, and C. J. Howard, J. Phys. Chem. **94**, 5839 (1990).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CH_3SSO + NO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.5 \pm 1.2) \times 10^{-12}$	297	Dominé, Murrells, and Howard, 1990[1]	(a)
Reviews and Evaluations			
4.5×10^{-12}	298	NASA, 1994[2]	(b)

Comments

(a) Fast-flow discharge system with photoionization mass spectrometric detection of products. CH_3SSO radicals were produced by $CH_3SS + NO_2 \rightarrow CH_3SSO + NO$. Mass 47 peak was monitored in excess NO_2 and the contributions from CH_3S and CH_3SSO (from $CH_3SSO + h\nu \rightarrow CH_3S^+ + e^- + SO$) separated by modeling using data from other mass peaks.

(b) Accepted the value of Dominé *et al.*[1]

Preferred Values

$k = 4.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The study of Dominé *et al.*[1] has provided the only available value for the rate coefficient of this reaction. This value is accepted but with substantial error limits until confirmatory studies are made.

References

[1] F. Dominé, T. P. Murrells, and C. J. Howard, J. Phys. Chem. **94**, 5839 (1990).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$O_3 + CH_3SCH_3 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k < 1 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based upon the sole study of Martinez and Herron,[1] and is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] R. I. Martinez and J. T. Herron, Int. J. Chem. Kinet. **10**, 433 (1978).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

OCS + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
OCS + $h\nu \rightarrow$ CO + S(^{3}P) (1)	308	388
$\rightarrow$ CO + S(^{1}D) (2)	419	286

Quantum yield data ($\phi=\phi_1+\phi_2$)

Measurement	Wavelength region	Reference	Comments
$\phi_1/\phi_2 = 0.055$	222	Nan, Burak, and Houston, 1993[1]	(a)

Comments

(a) Pulsed laser photolysis of OCS at 222 nm. Doppler profile of S($^3P_2$) was monitored by LIF at 147 nm. CO used to quench S(^{1}D). S($^3P_2$) yield of 0.050 relative to S(^{1}D) obtained. S($^3P_1$) and S($^3P_0$) were not monitored but if they were present in statistical amounts then total triplet yield =0.055. This work supersedes the earlier study[2] where a yield of 0.02 was obtained.

Preferred Values

	10^{21} σ/cm^2			
λ/nm	295 K	225 K	ϕ	ϕ_2
300	0.0009			
295	0.0023	0.0013		
290	0.0077	0.0035		
285	0.0218	0.0084		
280	0.0543	0.0206		
275	0.1504	0.0607		
270	0.376	0.156		
265	0.960	0.423		
260	2.52	1.16	0.8	0.6
255	6.64	3.46	0.8	0.6
250	16.5	9.79	0.8	0.6
245	38.2	25.1	0.8	0.6
240	81.3	59.3	0.8	0.6
235	153.6	123.7	0.8	0.6
230	243.8	211.8	0.8	0.6
225	310.4	283.0	0.8	0.6
220	304.8	287.5	0.8	0.6
215	241.6	236.2	0.8	0.6
210	150.8	151.6		
205	82.0	82.5		
200	39.3	39.3		
195	20.2	18.9		
190	39.7	26.8		
185	190.3	135.7		

Comments on Preferred Values

There is good agreement among all of the recent cross-section measurements for $\lambda<280$ nm.[2–4] At $\lambda>280$ nm the data of Molina *et al.*[2] appear to be the most accurate. The higher values in Ref. 1 may be due to the presence of CS_2 or other unidentified trace contaminants or alternatively dimerization of OCS in the pressurized cell employed. The preferred values are 5 nm averages based on the Molina *et al.* data.[2] The results of Locker *et al.*,[3] whose results were presented in graphical form, agree with these values.

The preferred overall quantum yield of 0.80 is an average of the results of Rudolf and Inn[4] and the earlier work of Sidhu *et al.*[5] which gave slightly higher values ($\phi_1 + \phi_2=0.9$), with $\phi_2/\phi \geqslant 0.72$. Breckenridge and Taube[6] obtained $\phi_2/\phi=0.74\pm0.04$ and their results suggest strongly that S(^{3}P) production accounts for the balance. They did not, however, determine absolute values for the quantum yields. There is currently no evidence for fluorescence from OCS. This is difficult to reconcile with a photodissociation yield significantly less than unity.

The study of Nan *et al.*[1] of the triplet channel yield indicates that it is small but we make no recommendation for ϕ_1 at this stage.

References

[1] G. Nan, I. Burak, and P. L. Houston, Chem. Phys. Lett. **209**, 383 (1993).

[2] L. T. Molina, J. J. Lamb, and M. J. Molina, Geophys. Res. Lett. **8**, 1008 (1981).

[3] J. R. Locker, J. B. Burkholder, E. J. Bair, and H. A. Webster, J. Phys. Chem. **87**, 1864 (1983).

[4] R. N. Rudolf and E. C. Y. Inn, J. Geophys. Res. **86**, 9891 (1981).

[5] K. S. Sidhu, I. G. Csizmadia, O. P. Strausz, and H. E. Gunning, J. Am. Chem. Soc. **88**, 2412 (1966).

[6] W. H. Breckenridge and H. Taube, J. Chem. Phys. **53**, 1713 (1970).

$CS_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CS_2 + h\nu \rightarrow CS_2^*$	(1)		>277
$\rightarrow CS + S(^3P)$	(2)	432	281
$\rightarrow CS + S(^1D)$	(3)	543	223

Absorption cross-section data

Wavelength range/nm	Reference	Comments
271–374	Hearn and Joens, 1991[1]	(a)

Comments

(a) Spectral resolution 0.06 nm. Deuterium lamp was used as source but results checked using atomic lines (narrow band width) from argon-mercury lamp and by measurements at 260 nm on the well characterized benzene spectrum. Results presented in graphical form in paper but authors provide data points at 0.02 nm intervals on request.

Preferred Values

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
295	10	335	6.0
305	35	345	3.0
315	62	355	0.8
325	37		

Quantum Yields

$\phi_{OCS} = 1.2 \times 10^{-2}$ for 290–360 nm region in 1 bar air.

Comments on Preferred Values

The recent measurements of Hearn and Joens[1] on the absorption spectrum were carried out using similar conditions of temperature, resolution, pathlength, and gas pressure to those used by Wu and Judge.[2] In both cases the resolution used (0.06 nm) is higher than in the study of Wine *et al.*[3] (0.4 nm). All of the studies[1–4] confirm the banded nature of the spectrum (280–370 nm). The values of the cross-section obtained by Hearn and Joens[1] are some 10–15% higher than those obtained by Wu and Judge[2] and there are minor differences in the band structures observed. When the data of Hearn and Joens are averaged over 10 nm intervals the mean absorption coefficients are in reasonable agreement with our previous recommendations which were based on unpublished data from the AERE Laboratories, Harwell. The preferred values given are mean values of the Harwell results and those of Hearn and Joens.[1]

The recommended quantum yield for OCS production from the photoinitiated oxidation of CS_2 in air is that reported by Jones *et al.*,[4] which is in good agreement with the value estimated by Wine *et al.*[3] from the earlier data of Wood and Heicklen[5] (i.e., ϕ_{OCS}=0.01–0.015). The recommended value might best be considered an upper limit since the observed slow oxidation of the CS_2 could have been due, at least in part, to other mechanisms.

Since there is insufficient energy to dissociate CS_2 at $\lambda < 281$ nm the photochemical reaction yielding OCS and SO_2, studied by Jones *et al.*[4] in the range 290–360 nm and others,[5,6] must arise from reactions involving excited CS_2 molecules.

References

[1] C. H. Hearn and J. A. Joens, J. Quant. Spectrosc. Radiat. Trans. **45**, 69 (1991).

[2] C. Y. R. Wu and D. L. Judge, Geophys. Res. Lett. **8**, 769 (1981).

[3] P. H. Wine, W. L. Chameides, and A. R. Ravishankara, Geophys. Res. Lett. **8**, 543 (1981).

[4] B. M. R. Jones, R. A. Cox, and S. A. Penkett, J. Atmos. Chem. **1**, 65 (1983).

[5] W. P. Wood and J. Heicklen, J. Phys. Chem. **75**, 854 (1971).

[6] M. DeSorgo, A. J. Yarwood, O. P. Strausz, and H. E. Gunning, Can. J. Chem. **43**, 1886 (1965).

$CH_3SSCH_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$CH_3SSCH_3 \rightarrow CH_3SS + CH_3$	(1)	238	502
$\rightarrow 2CH_3S$	(2)	274	437

No new data have been published since our last evaluation.

Preferred Values

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²
201	1053.0	280	49.8
205	850.0	285	36.0
210	630.0	290	25.15
215	312.0	295	17.06
220	138.7	300	11.27
225	85.6	305	7.24
228 (min)	82.3	310	4.57
230	84.2	315	2.85
235	96.0	320	1.79
240	110.0	325	1.09
245	120.7	330	0.67
250	125.4	335	0.38
251 (max)	125.6	340	0.22
255	123.3	345	0.14
260	113.9	350	0.07
265	99.3	355	0.04
270	82.7	360	<0.01
275	65.4		

Comments on Preferred Values

The preferred values for σ are those of Hearn *et al.*[1] which agree well with the earlier values cited in Calvert and Pitts.[2] Sheraton and Murray's spectrum[3] agrees qualitatively with the other studies but the reported absorption coefficients are significantly lower.

The thermochemistry suggests that formation of CH_3S is the sole dissociation process at wavelengths of importance to atmospheric photochemistry. Balla and Heicklen[4] report a quantum yield for CH_3S formation of 2.04±0.06 for light absorption in the range 280–300 nm, but as yet there are no definitive measurements of the quantum yields.

References

[1] C. H. Hearn, E. Turcu, and J. A. Joens, Atmos. Environ. **24A**, 1939 (1990).

[2] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966), p. 490.

[3] D. F. Sheraton and F. E. Murray, Can J. Chem. **59**, 2750 (1981).

[4] R. J. Balla and J. Heicklen, Can. J. Chem. **62**, 162 (1984).

$CH_3SNO + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$CH_3SNO \rightarrow CH_3S + NO$	(1)	-	-
$\rightarrow CH_3 + SNO$	(2)	-	-

No new data have been published since our last evaluation.

Preferred Values

λ/nm	10^{19} σ/cm^2	λ/nm	10^{19} σ/cm^2
190	5	310	14.9
195	104	320	18.5
200 (max)	162	330	21.3
205	91	335 (max)	21.6
210 (min)	81	340	21.5
215	98	350	19.6
218 (max)	104	360	16.5
220	96	370	12.7
225	73	380	9.6
230	40	390	6.7
240	16	400	4.5
250	3.5	410	2.9
260	1.7	420	2.0
264 (min)	1.5	430	1.3
270	1.8		
280	2.7	510	0.24
290	5.2	545	0.58
300	9.3		

Comments on Preferred Values

The spectrum of CH_3SNO consists of a weak transition in the 500–600 nm region showing some vibrational fine structure and stronger continuous bands at shorter wavelengths.[1] The CH_3S-NO dissociation energy has been estimated[2] to be approximately 110 kJ mol^{-1} but because more reliable data are not available we do not give wavelength limits for the dissociation channels tabulated.

The only available data for σ values in the gas phase appear to be those of Niki *et al.*[3] who have published their results mainly in the form of graphs covering the range 190–430 nm. Their published spectrum shows no fine structure but appears to consist of overlapping continua with three maxima at approximately 200, 218, and 335 nm. The preferred values of σ in the range 190–430 nm are taken from the graphs of Niki *et al.*[3] and cannot be considered to be very precise. The two values at 510 and 545 nm are numerical values quoted in the same study.

There have been no quantum yield measurements. By analogy with CH_3ONO photolysis the primary products are expected to be CH_3S and NO. This is supported by the work of McCoustra and Pfab[1] who studied the photodissociation of CH_3SNO in a molecular beam and by the study of Niki *et al.*[3] who found CH_3SSCH_3 and NO to be the only major products from CH_3SNO photolysis at 300–400 nm.

References

[1] M. R. S. McCoustra and J. Pfab, Chem. Phys. Lett. **137**, 355 (1987).

[2] S. W. Benson, Chem. Rev. **78**, 23 (1978).

[3] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **87**, 7 (1983).

4.6. Fluorine Species

$O + FO \rightarrow O_2 + F$

$\Delta H° = -279$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.7\pm0.2)\times10^{-11}$	298	Bedzhanyan *et al.*, 1993[1]	(a)
Reviews and Evaluations			
5×10^{-11}	298	IUPAC, 1992[2]	(b)
2.7×10^{-11}	200–300	NASA, 1994[3]	(c)

Comments

(a) Discharge flow system. Pseudo-first-order decays of FO radicals in the presence of excess O(^{3}P) atoms were monitored by LMR. [O] determined by EPR.

(b) Estimated value.

(c) Based on the results of Bedahanyan *et al.*[1]

Preferred Values

$k = 2.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the results of the recent study of Bedzhanyan *et al.*,[1] the sole study of this reaction. The temperature dependence of the rate constant is expected to be small for such an atom-radical process, as for the analogous ClO radical reaction.

References

[1] Yu. R. Bedzhanyan, E. M. Markin, G. G. Politenkova, and Yu. M. Gershenzon, Kinetics and Catalysis **38**, 797 (1993); original pages 998–1003 (1992).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$O + FO_2 \rightarrow O_2 + FO$

$\Delta H° = -166$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.7$ at 298 K.

Comments on Preferred Values

There are no experimental data for this reaction. The rate constant for such a radical-atom process is expected to approach the gas collision frequency and is not expected to exhibit a strong temperature dependence. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.[1]

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O(^1D) + HF \rightarrow HO + F \quad (1)$
$\rightarrow O(^3P) + HF \quad (2)$

$\Delta H°(1) = -46.9$ kJ·mol^{-1}
$\Delta H°(2) = -189.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2$)

$k=1\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.5$ at 298 K.

Comments on Preferred Values

There are no published experimental data for this reaction. k is assumed to be comparable to most other O(^{1}D) atom rate constants which approach the gas kinetic collision frequency, and as such is not expected to exhibit a strong temperature dependence. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.[1]

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O(^1D) + COF_2 \rightarrow CO_2 + F_2$ (1)

$\rightarrow O(^3P) + COF_2$ (2)

$\Delta H°(1)=-197.7$ kJ·mol^{-1}
$\Delta H°(2)=-189.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k_1=2.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2=5.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k_1=\Delta\log k_2=\pm0.2$ at 298 K.

Comments on Preferred Values

The preferred values for k_1 and k_2 are based on the results reported in the study of Wine and Ravishankara,[1] which is much more direct than the other studies. Both the overall rate and the branching ratio reported in this study[1] are accepted. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[2]

References

[1] P. H. Wine and A. R. Ravishankara, Chem. Phys. Lett. **96**, 129 (1983).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O(^1D)$ + HFC's → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.0×10^{-10} CH_3CHF_2 4.9×10^{-11} CH_2FCF_3 1.2×10^{-10} CHF_2CF_3	298	Warren, Gierczak, and Ravishankara, 1991[1]	(a)
1.6×10^{-10} CH_3F 5.1×10^{-11} CH_2F_2 9.8×10^{-12} CHF_3 2.6×10^{-10} CH_3CH_2F	298	Schmoltner *et al.*, 1993[2]	(a)
Reviews and Evaluations			
1.4×10^{-10} CH_3F 9×10^{-11} CH_2F_2 8.4×10^{-12} CHF_3 1×10^{-10} CH_3CHF_2 1×10^{-10} CH_3CF_3 1×10^{-10} CH_2FCF_3 5×10^{-11} CHF_2CF_3	298	IUPAC, 1992[3]	(b)
1.5×10^{-10} CH_3F 5.1×10^{-11} CH_2F_2 9.1×10^{-12} CHF_3 2.6×10^{-10} CH_3CH_2F 2.0×10^{-10} CH_3CHF_2 1.0×10^{-10} CH_3CF_3 4.9×10^{-11} CH_2FCF_3 1.2×10^{-10} CHF_2CF_3	200–300	NASA, 1994[4]	(c)

Comments

(a) Laser flash photolysis of O_3 at 248 nm. Time-resolved production of $O(^3P)$ atoms was monitored by resonance fluorescence at 130 nm.

(b) CH_3F and CHF_3—based on results of Force and Wiesenfeld.[5] CH_2F_2, CH_3CF_3, and CH_2FCF_3—based on results of Green and Wayne.[6] CH_3CHF_2, and CH_2FCF_3—estimated by analogy.

(c) (c) CH_3F and CHF_3—based on results of Schmoltner *et al.*[2] and Force and Wiesenfeld.[5] CH_2F_2 and CH_3CH_2F—based on results of Schmoltner *et al.*[2] CH_3CF_3—based on results of Green and Wayne.[6] CH_3CHF_2, CH_2FCF_3, and CHF_2CF_3—based on results of Warren *et al.*[1]

Preferred Values

CH_3F	$k=1.6\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CH_2F_2	$k=5.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CHF_3	$k=9.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CH_3CH_2F	$k=2.6\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CH_3CHF_2	$k=2.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CH_3CF_3	$k=1.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CH_2FCF_3	$k=4.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CHF_2CF_3	$k=1.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K for CH_3F.

$\Delta\log k=\pm0.3$ at 298 K for CH_2F_2, CHF_3, CH_3CH_2F, CH_3CHF_2, CH_3CF_3, CH_2FCF_3, and CHF_2CF_3.

Comments on Preferred Values

The rate coefficients given are for the total disappearance of $O(^1D)$ atoms and include both physical quenching and chemical reaction. Because these rate coefficients have such high values (nearly collisional) at 298 K, they can be assumed to be temperature-independent. Specific comments are as follows:

CH_3F	Based on results of Schmoltner *et al.*[2] who also report 11% physical quenching. Good agreement with results of Force and Wiesenfeld.[5]
CH_2F_2	Based on results of Schmoltner *et al.*[2] who also report 70% physical quenching.
CHF_3	Based on results of Schmoltner *et al.*[2] who also report essentially complete physical quenching. Good agreement with the results of Force and Wiesenfeld.[5]
CH_3CH_2F	Based on results of Schmoltner *et al.*[2] who also report 18% physical quenching.
CH_3CHF_2	Based on results of Warren *et al.*[1] who also report 54% physical quenching.
CH_3CF_3	Based on results of Green and Wayne.[6]
CH_2FCF_3	Based on results of Warren *et al.*[1] who also report 94% physical quenching.
CHF_2CF_3	Based on results of Warren *et al.*[1] who also report 85% physical quenching.

References

[1] R. Warren, T. Gierczak, and A. R. Ravishankara, Chem. Phys. Lett. **183**, 403 (1991).
[2] A. M. Schmoltner, R. K. Talukdar, R. F. Warren, A. Mellouki, L. Goldfarb, T. Gierczak, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **97**, 8976 (1993).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] A. P. Force and J. R. Wiesenfeld, J. Phys. Chem. **85**, 782 (1981).
[6] R. G. Green and R. P. Wayne, J. Photochem. **6**, 371 (1976).

$F + H_2 \rightarrow HF + H$

$\Delta H° = -134.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.4 \times 10^{-10}$ exp$(-500/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–375 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The value of k at 298 K seems to be well established, with the results reported by Zhitneva and Pshezhetskii,[1] Heidner *et al.*,[2] Wurzberg and Houston,[3] Dodonov *et al.*,[4] Clyne *et al.*,[5] Igoshin *et al.*,[6] Clyne and Hodgson,[7] and Stevens *et al.*[8] being in good agreement; the preferred value at 298 K is the mean of these values. Reported values of E/R range from 433–595 K (Refs. 2, 3, 6, and 8). The preferred value of E/R is derived from a least-squares fit to the data in these studies, and the A-factor was chosen to fit the recommended room temperature value. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[9]

References

[1] G. P. Zhitneva and S. Ya. Pshezhetskii, Kinetika i Katalia **19**, 296 (1978).
[2] R. F. Heidner, J. F. Bott, C. E. Gardner, and J. E. Melzer, J. Chem. Phys. **72**, 4815 (1980).
[3] E. Wurzberg and P. L. Houston, J. Chem. Phys. **72**, 4811 (1980).
[4] A. F. Dodonov, G. K. Lavrovskaya, I. I. Morozov, and V. L. Tal'Roze, Dokl. Akad. Nauk **198**, 622 (1971).
[5] M. A. A. Clyne, D. J. McKenney, and R. F. Walker, Can. J. Chem. **51**, 3596 (1973).
[6] V. I. Igoshin, L. V. Kulakov, and A. I. Nikitin, Sov. J. Quantum Electron. **3**, 306 (1974).
[7] M. A. A. Clyne and A. Hodgson, J. Chem. Soc. Faraday Trans. 2, **81**, 443 (1985).
[8] P. S. Stevens, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **93**, 4068 (1989).
[9] IUPAC, Supplement IV, 1992 (see references in Introduction).

$F + H_2O \rightarrow HF + HO$

$\Delta H° = -71.6$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 240–370 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The recommended temperature-independent value is based on the results reported by Stevens *et al.*[1] This value is in good agreement with the room temperature results of Frost *et al.*[2] and Walther and Wagner.[3] The latter authors[3] in a limited temperature study reported an E/R value of 400 K. Although these data have not been used in derivation of the preferred value, with the exception of the one low temperature data point they are within the stated uncertainty limit. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] P. S. Stevens, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **93**, 4068 (1989).
[2] R. J. Frost, D. S. Green, M. K. Osborn, and I. W. M. Smith, Int. J. Chem. Kinet. **18**, 885 (1986).
[3] C. D. Walther and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **87**, 403 (1983).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$F + O_2 + M \rightarrow FO_2 + M$

$\Delta H^\circ = -53.3$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.4×10^{-32} [SF_6]	295	Ellermann *et al.*, 1994[1]	(a)
5.8×10^{-33} $(T/300)^{-1.7}$ [N_2]	100–373	Campuzano-Jost *et al.*, 1995[2]	(b)
Reviews and Evaluations			
3.7×10^{-33} $(T/300)^{-1}$ [N_2]	300–400	IUPAC, 1992[3]	(c)
4.4×10^{-33} $(T/300)^{-1.2}$ [air]	200–300	NASA, 1994[4]	(d)

Comments

(a) Pulse radiolysis of SF_6-O_2 mixtures at 200–1000 Torr total pressure with kinetic UV spectroscopy detection of FO_2 radicals between 215–254 nm. Falloff extrapolations were made with $F_c=0.6$.

(b) Flash photolysis system with UV absorption of FO_2 radicals. Experiments were carried out between 100 and 373 K, and up to 1000 bar, and in the bath gases He, Ar, and N_2. Measurements of the equilibrium constant lead to $\Delta H^\circ = -50.8$ kJ mol^{-1}. Falloff extrapolations were made with F_c near 0.5.

(c) Average of the data of Refs. 5 and 6. It was assumed that k_0 is similar for M=Ar and N_2.

(d) Based on the study of Pagsberg *et al.*,[5] which is in agreement with previous measurements.

Preferred Values

$k_0=5.8\times10^{-33}$ $(T/300)^{-1.7}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 100–400 K.

Reliability

$\Delta\log k_0 = \pm0.3$ at 298 K.

$\Delta n = \pm0.5$.

Comments on Preferred Values

Because of the large data base of Ref. 2, these values are preferred and are in reasonable agreement with earlier work. Falloff curves were constructed with F_c near 0.5.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.0×10^{-12}	295	Ellermann *et al.*, 1994[1]	(a)
1.2×10^{-10}	100–373	Campuzano-Jost *et al.*, 1995[2]	(b)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

Preferred Values

$k_\infty=1.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 100–400 K.

Reliability

$\Delta\log k_\infty = \pm0.3$ over the range 100–400 K.

Comments on Preferred Values

Because of the large pressure range studied in Ref. 2, a reliable falloff extrapolation towards k_∞ was possible. The data of Ref. 2, therefore, are preferred together with values of F_c near 0.5.

Intermediate falloff range

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	P/Torr	M	Temp./K	Reference	Comments
Relative Rate Coefficients					
2.4×10^{-13}	585 mbar	SF_6	298	Wallington and Nielsen, 1991[7]	(a)
$(2.35\pm0.2)\times10^{-13}$	600 mbar	SF_6	298	Wallington *et al.*, 1992[8]	(b)

Comments

(a) Pulse radiolysis of a mixture of SF_6 and O_2 (6.1–20 mbar). FO_2 radicals were monitored by UV absorption at 220 nm.

(b) Pulse radiolysis of a mixture of SF_6 and O_2 (2.5–15 mbar). FO_2 radicals were monitored by UV absorption at 220 nm. The results were analyzed together with those of Ref. 6.

References

[1] T. Ellermann, J. Sehested, O. J. Nielsen, P. Pagsberg, and T. J. Wallington, Chem. Phys. Lett. **218**, 287 (1994).
[2] P. Campuzano-Jost, A. E. Croce, H. Hippler, M. Siefke, and J. Troe, J. Chem. Phys. **102**, 5317 (1995).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] P. Pagsberg, E. Ratajczak, A. Sillesen, and J. T. Jodkowski, Chem. Phys. Lett. **141**, 88 (1987).
[6] J. L. Lyman and R. Holland, J. Phys. Chem. **92**, 7232 (1988).
[7] T. J. Wallington and O. J. Nielsen, Int. J. Chem. Kinet. **23**, 785 (1991).
[8] T. J. Wallington, M. M. Maricq, T. Ellermann, and O. J. Nielsen, J. Phys. Chem. **96**, 982 (1992).

$FO_2 + M \rightarrow F + O_2 + M$

$\Delta H° = 53.3$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.0\times10^{-5}\ T^{-1.25}\exp(-5990/T)\ [N_2]$	315–420	Campuzano-Jost *et al.*, 1995[1]	(a)
Reviews and Evaluations			
$2.2\times10^{-17}\ [N_2]$	298	IUPAC, 1989[2]	(b)

Comments

(a) Flash photolysis/UV absorption study monitoring FO_2 radicals. Experiments were carried out between 100 and 375 K at total pressures between 1 and 1000 bar, and in the bath gases He, Ar, and N_2. Measurements of the equilibrium constant lead to $\Delta H° = -49.8$ kJ mol^{-1}. Falloff extrapolations were carried out with a value of F_c near 0.5. The expression for k_0 was derived from the recombination rate coefficients of the reverse reaction and the equilibrium constants.

(b) Based on the experiments of Ref. 3.

Preferred Values

$k_0 = 1.5\times10^{-17}\ [N_2]\ s^{-1}$ at 298 K.

$k_0 = 8.4\times10^{-9}\ (T/300)^{-1.25}\exp(-5990/T)\ [N_2]\ s^{-1}$ over the temperature range 315–420 K.

Reliability

$\Delta\log k_0 = \pm0.3$ at 298 K.

$\Delta n = \pm0.5$.

$\Delta(E/R) = \pm500$ K.

Comments on Preferred Values

The results of Ref. 1 are in reasonable agreement with those of Ref. 3 but differ at 298 K by a factor of 6 with the data from Ref. 4. The preferred values are based on the data of Ref. 1.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.3\times10^{13}\ T^{0.45}\exp(-5990/T)$	315–420	Campuzano-Jost *et al.*, 1995[1]	(a)

Comments

(a) See comment (a) for k_0.

Preferred Values

$k_\infty=3.1\times10^{5}$ s^{-1} at 298 K.

$k_\infty=1.7\times10^{14}\ (T/300)^{0.45}\exp(-5990/T)$ s^{-1} over the temperature range 315–420 K.

Reliability

$\Delta\log k_\infty=\pm0.3$ at 300 K.

$\Delta n=\pm0.5$.

$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

Because of the large pressure range studied in Ref. 1, a reliable falloff extrapolation towards k_∞ was possible. The data of Ref. 1, therefore, are preferred together with F_c values near 0.5.

References

[1] P. Campuzano-Jost, A. E. Croce, H. Hippler, M. Siefke, and J. Troe, J. Chem. Phys. **102**, 5317 (1995).

[2] IUPAC, Supplement III, 1989 (see references in Introduction).

[3] P. Pagsberg, E. Ratajczk, A. Sillesen, and J. T. Jodkowski, Chem. Phys. Lett. **141**, 88 (1987).

[4] J. L. Lyman and R. Holland, J. Phys. Chem. **92**, 7232 (1988).

$F + O_3 \rightarrow FO + O_2$

$\Delta H^\circ=-113$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.8\times10^{-11}\exp[-(226\pm200)/T]$	253–365	Wagner, Zetzsch, and Warnatz, 1972[1]	(a)
1.3×10^{-11}	298		
$(6.2\pm0.3)\times10^{-12}$	298	Bedzhanyan, Markin, and Gershenzon, 1993[2]	(b)
Reviews and Evaluations			
$2.8\times10^{-11}\exp(-230/T)$	250–365	IUPAC, 1992[3]	(c)
$2.2\times10^{-11}\exp(-230/T)$	250–365	NASA, 1994[4]	(d)

Comments

(a) Discharge flow system with MS detection of O_3 decay in excess F atoms. Temporal profiles of F, FO, and O_3 monitored by MS.

(b) Discharge flow system with excess of O_3 over F atoms. Rate of formation of FO radicals monitored by LMR.

(c) Based on the data of Wagner *et al.*[1]

(d) Based on the data of Wagner *et al.*[1] and Bedzhanyan *et al.*[2]

Preferred Values

$k=1.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=2.2\times10^{-11}\exp(-230/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–365 K.

Reliability

$\Delta\log k=\pm0.25$ at 298 K.

$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The preferred room temperature value is the average of the room temperature values from the two studies.[1,2] The temperature dependence is taken from Wagner *et al.*[1] and the *A*-factor is fitted to the preferred room temperature value. The value appears to be quite reasonable by analogy with the reactivity of atomic chlorine with ozone.

References

[1] H. Gg. Wagner, C. Zetzsch, and J. Warnatz, Ber. Bunsenges. Phys. Chem. **76**, 526 (1972).

[2] Yu. R. Bedzhanyan, E. M. Markin, and Yu. M. Gershenzon, Kinetics and Catalysis **33**, 594 (1993); original pages 744–752 (1992).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

$F + HONO_2 \rightarrow HF + NO_3$

$\Delta H^\circ = -143.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.7\pm0.5)\times10^{-11}$	298	Mellouki, Le Bras, and Poulet, 1987[1]	(a)
$(2.1\pm1)\times10^{-11}$	298	Rahman *et al.*, 1988[2]	(b)
$6.0\times10^{-12}\exp[(400\pm120)/T]$	260–320	Wine, Wells, and Nicovich, 1988[3]	(c)
$(2.3\pm0.1)\times10^{-11}$	298		
$(2.2\pm0.2)\times10^{-11}$	298	Becker *et al.*, 1991[4]	(d)
Reviews and Evaluations			
$6.0\times10^{-12}\exp(400/T)$	260–320	IUPAC, 1992[5]	(e)
$6.0\times10^{-12}\exp(400/T)$	200–300	NASA, 1994[6]	(e)

Comments

(a) Discharge flow system with EPR detection of F atoms.

(b) Discharge flow system with MS detection of HF, NO_3 radicals and HNO_3.

(c) Pulsed laser photolysis at 351 nm with long-path laser absorption of NO_3 at 662 nm. At higher temperatures (335–373 K) the rate coefficient was found to be independent of temperature with a value of $(2.0\pm0.3)\times10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(d) Two separate discharge flow systems with different detectors. In one system the formation of NO_3 as a function of time was measured by MS; in the other system, the decay of F atoms as a function of time was measured by EPR.

(e) Based on results of the temperature-dependent study of Wine *et al.*,[3] and the room temperature results of Mellouki *et al.*[1] and Rahman *et al.*[2]

Preferred Values

$k = 2.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.0\times10^{-12}\exp(400/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–320 K.

Reliability

$\Delta\log k = \pm0.1$ at 298 K.

$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

The recommendation is based on the results of the temperature-dependent study of Wine *et al.*[3] and the room temperature results of Mellouki *et al.*,[1] Rahman *et al.*,[2] and Becker *et al.*[4] The values at room temperature are in good agreement. The study of Wine *et al.*[3] was over the temperature range 260–373 K; below 320 K the authors fitted their data with the Arrhenius expression recommended here, whereas at higher temperatures a temperature-independent value was found, suggesting the occurrence of different mechanisms in the two temperature regimes.

References

[1] A. Mellouki, G. Le Bras, and G. Poulet, J. Phys. Chem. **91**, 5760 (1987).

[2] M. M. Rahman, E. Becker, Th. Benter, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **92**, 91 (1988).

[3] P. H. Wine, J. R. Wells, and J. M. Nicovich, J. Phys. Chem. **92**, 2223 (1988).

[4] E. Becker, Th. Benter, R. Kampf, R. N. Schindler, and U. Wille, Ber. Bunsenges. Phys. Chem. **95**, 1168 (1991).

[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

[6] NASA Evaluation No. 11, 1994 (see references in Introduction).

$F + CH_4 \rightarrow HF + CH_3$

$\Delta H^\circ = -131.9$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 8.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.0\times10^{-10}\exp(-400/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–450 K.

Reliability

$\Delta\log k = \pm0.2$ at 298 K.

$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

The preferred values are based on the room-temperature results of Clyne *et al.*,[1] Kompa and Wanner,[2] Pollock and

Jones,[3] and Fasano and Nogar,[4] the 298–450 K results of Wagner *et al.*,[5] and the 253–348 K results of Foon and Reid.[6] These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[7]

References

[1] M. A. A. Clyne, D. J. McKenney, and R. F. Walker, Can. J. Chem. **51**, 3596 (1973).

[2] K. L. Kompa and J. Wanner, Chem. Phys. Lett. **12**, 560 (1972).

[3] T. L. Pollock and W. E. Jones, Can. J. Chem. **51**, 2041 (1973).

[4] D. M. Fasano and N. S. Nogar, Chem. Phys. Lett. **92**, 411 (1982).

[5] H. Gg. Wagner, J. Warnatz, and C. Zetzsch, An. Assoc. Quim. Argentina **59**, 169 (1971).

[6] R. Foon and G. P. Reid, Trans. Faraday Soc. **67**, 3513 (1971).

[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CH_3F$ (HFC-41) $\rightarrow H_2O + CH_2F$

$\Delta H° = -80.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.75\times10^{-12}\exp[-(1300\pm100)/T]$	243–373	Schmoltner *et al.*, 1993[1]	(a)
$(2.23\pm0.38)\times10^{-14}$	298		
Relative Rate Coefficients			
$(1.61\pm0.08)\times10^{-14}$	296±2	Wallington and Hurley, 1993[2]	(b)
$(1.36\pm0.07)\times10^{-14}$	296±2	Wallington and Hurley, 1993[2]	(c)
$1.96\times10^{-18}\,T^2\exp[-(634\pm35)/T]$	298–363	Hsu and DeMore, 1995[3]	(d)
1.95×10^{-14}	298		
Reviews and Evaluations			
$3.7\times10^{-12}\exp(-1600/T)$	270–340	IUPAC, 1992[4]	(e)
$5.51\times10^{-18}\,T^2\exp(-1005/T)$	292–480	Atkinson, 1994[5]	(f)
$3.0\times10^{-12}\exp(-1500/T)$	243–373	NASA, 1994[6]	(g)

Comments

(a) Pulsed laser photolysis system with LIF detection of HO radicals.

(b) Relative rate method. HO radicals were generated by photolysis of CH_3ONO at 700 Torr total pressure of air. The decay of CH_3F was inferred from the measured formation of HC(O)F, using a formation yield of HC(O)F of 0.90 as measured in separate Cl_2-CH_3F-NO-air irradiations. The concentrations of HC(O)F and acetylene were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3F)/k(HO + C_2H_2) = 0.0201\pm0.0009$ was placed on an absolute basis by using $k(HO + C_2H_2) = 7.99\times10^{-13}$ cm^3 molecule^{-1} s^{-1}.[5,7]

(c) HO radicals generated by the photolysis of O_3 at 254 nm in the presence of H_2. The concentrations of CH_4 and CH_3F were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3F)/k(HO + CH_4) = 2.30\pm0.11$ was placed on an absolute basis by using $k(HO + CH_4) = 5.92\times10^{-15}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or O_3-H_2O)-CH_3F-CH_3CHF_2-O_2-N_2 mixtures. The concentrations of CH_3F and CH_3CHF_2 were measured by IR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3F)/k(HO + CH_3CHF_2) = (0.99\pm0.10)\exp[-(174\pm34)/T]$ is placed on an absolute basis by using a rate coefficient of $k(HO + CH_3CHF_2) = 1.98\times10^{-18}\,T^2\exp(-460/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) The absolute rate coefficients of Howard and Evenson,[8] Nip *et al.*,[9] and Jeong and Kaufman[10,11] were fitted to the three-parameter equation $k = CT^2\exp(-D/T)$, resulting in $k = 5.51\times10^{-18}\,T^2\exp(-1005/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 292–480 K. The Arrhenius expression $k = A\exp(-B/T)$, is centered at 300 K and is derived from the three-parameter equation with $A = C\,e^2\,T^2$ and $B = D + 2T$.

(f) Derived from the absolute rate coefficient data of Howard and Evenson,[8] Nip *et al.*,[9] and Jeong and Kaufman.[10,11]

(g) Derived from the absolute rate coefficients of Howard and Evenson,[8] Nip *et al.*,[9] and Schmoltner *et al.*[1] and the relative rate coefficients of Hsu and DeMore.[3]

Preferred Values

$k = 2.0\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.6\times10^{-12}\exp(-1305/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values

The absolute laser photolysis-LIF rate coefficients of Schmoltner *et al.*[1] are higher than those reported previously by Jeong and Kaufman,[10,11] although the discrepancy decreases with increasing temperature. The absolute rate coefficients of Schmoltner *et al.*[1] exhibit a significant amount of scatter at temperatures ≤ 273 K, for unknown reasons. Since secondary reactions of HO radicals with CH_2F radicals and other radical species were expected to have occurred in the study of Bera and Hanrahan,[12] the rate coefficient of Bera and Hanrahan[12] was not used in the evaluation. The absolute rate coefficients of Howard and Evenson,[8] Nip *et al.*,[9] Jeong and Kaufman,[10,11] and Schmoltner *et al.*[1] were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 3.14 \times 10^{-18}\ T^2 \exp(-776/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 243–480 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = C\ e^2\ T^2$ and $B = D + 2T$. The relative rate coefficients of Hsu and DeMore[3] agree with the preferred values to within 8% over the temperature range 298–363 K.

References

[1] A. M. Schmoltner, R. K. Talukdar, R. F. Warren, A. Mellouki, L. Goldfarb, T. Gierczak, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **97**, 8976 (1993).

[2] T. J. Wallington and M. D. Hurley, Environ. Sci. Technol. **27**, 1448 (1993).

[3] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

[5] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[6] NASA Evaluation No. 11, 1994 (see references in Introduction).

[7] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 1**, 1 (1989).

[8] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).

[9] W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. **83**, 2440 (1979).

[10] K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).

[11] K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. **88**, 1222 (1984).

[12] R. K. Bera and R. J. Hanrahan, Radiat. Phys. Chem. **32**, 579 (1988).

$HO + CH_2F_2$ (HFC-32) $\rightarrow H_2O + CHF_2$

$\Delta H^\circ = -67.0$ kJ·mol⁻¹

Rate coefficient data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comment
Absolute Rate Coefficients			
$(2.52 \pm 0.25) \times 10^{-15}$	223	Schmoltner *et al.*, 1993[1]	(a)
$(1.09 \pm 0.03) \times 10^{-14}$	298		
Relative Rate Coefficients			
$1.58 \times 10^{-18}\ T^2 \exp[-(737 \pm 24)/T]$	297–383	Hsu and DeMore, 1995[2]	(b)
1.14×10^{-14}	297		
Reviews and Evaluations			
$2.0 \times 10^{-12} \exp(-1545/T)$	240–300	IUPAC, 1992[3]	(c)
$3.84 \times 10^{-18}\ T^2 \exp(-1016/T)$	222–492	Atkinson, 1994[4]	(d)
$1.9 \times 10^{-12} \exp(-1550/T)$	222–400	NASA, 1994[5]	(e)

Comments

(a) Pulsed photolysis system with LIF detection of HO radicals.

(b) Relative rate method. HO radicals were generated from the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or O_3-H_2O)-CH_2F_2-CH_3CHF_2-O_2-N_2 mixtures. The concentrations of CH_2F_2 and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_2F_2)/k(HO + CH_3CHF_2) = (0.80 \pm 0.06) \exp[-(277 \pm 24)/T]$ is placed on an absolute basis using a rate coefficient of $k(HO + CH_3CHF_2) = 1.98 \times 10^{-18}\ T^2 \exp(-460/T)$ cm³ molecule⁻¹ s⁻¹ (this evaluation).

(c) See Comments on Preferred Values.

(d) Derived from the absolute rate coefficient data of Howard and Evenson,[6] Nip *et al.*,[7] Jeong and Kaufman,[8] and Talukdar *et al.*[9]

(e) Derived from the rate coefficients of Howard and Evenson,[6] Nip *et al.*,[7] Jeong and Kaufman,[8] Talukdar *et al.*,[9] Schmoltner *et al.*,[1] and Hsu and DeMore[2] below 400 K.

Preferred Values

$k = 1.1 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

$k = 2.0 \times 10^{-12} \exp(-1545/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 240–300 K.

Reliability

$\Delta\log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Schmoltner *et al.*[1] at 223 K and 298 K are in excellent agreement with the earlier, and much more extensive, rate coefficient data of this research group (Talukdar *et al.*[9]). Accordingly, our previous evaluation, IUPAC, 1992,[3] is unchanged. The room temperature rate coefficients of Nip *et al.*,[7] Jeong and Kaufman,[8] Talukdar *et al.*,[9] and Schmoltner *et al.*[1] are in good agreement, but are ~30% higher than those of Howard and Evenson,[6] Clyne and Holt,[10] and Bera and Hanrahan.[11] The data of Clyne and Holt[10] are not considered reliable,[3,5] and that of Bera and Hanrahan[11] may have been subject to secondary reactions. The rate coefficients measured by Jeong and Kaufman[8] (250–492 K) and Talukdar *et al.*[9] (222–381 K) are in good agreement over the temperature range where they overlap. The rate coefficient data of Howard and Evenson,[6] Nip *et al.*,[7] Jeong and Kaufman,[8] and Talukdar *et al.*[9] have been fitted to the three parameter equation $k=CT^2\exp(-D/T)$, resulting in $k=3.84\times10^{-18}\ T^2\ \exp(-1016/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 222–492 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$, is centered at 265 K and is derived from the three-parameter equation with $A=C\,e^2\,T^2$ and $B=D+2T$.

The relative rate coefficients of Hsu and DeMore[2] are in good agreement with the recommended three parameter expression at room temperature, but are ~15% lower at 383 K (and the rate coefficients of Hsu and DeMore[2] extrapolated to 240 K lead to a rate coefficient which is 30% higher than that predicted from the recommended three parameter equation).

References

[1] A. M. Schmoltner, R. K. Talukdar, R. F. Warren, A. Mellouki, L. Goldfarb, T. Gierczak, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **97**, 8976 (1993).

[2] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

[6] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).

[7] W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. **83**, 2440 (1979).

[8] K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).

[9] R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **95**, 5815 (1991).

[10] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).

[11] R. K. Bera and R. J. Hanrahan, Radiat. Phys. Chem. **32**, 579 (1988).

$HO + CHF_3$ (HFC-23) $\rightarrow H_2O + CF_3$

$\Delta H^\circ = -50.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.93\times10^{-13}\exp[-(2300\pm100)/T]$	252–374	Schmoltner *et al.*, 1993[1]	(a)
$(3.08\pm0.28)\times10^{-16}$	298		
Relative Rate Coefficients			
$1.08\times10^{-18}\ T^2\exp[-(1780\pm44)/T]$	298–383	Hsu and DeMore, 1995[2]	(b)
2.40×10^{-16}	298		
Reviews and Evaluations			
$1.0\times10^{-12}\exp(-2490/T)$	270–340	IUPAC, 1992[3]	(c)
$1.49\times10^{-18}\ T^2\exp(-1887/T)$	387–1445	Atkinson, 1989;[4] Atkinson, 1994[5]	(d)
$1.5\times10^{-12}\exp(-2650/T)$	296–410	NASA, 1994[6]	(e)

Comments

(a) Pulsed laser photolysis system with LIF detection of HO radicals.

(b) Relative rate method. HO radicals were generated from the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or H_2O-O_3)-CHF_3-CHF_2CF_3-N_2-O_2 mixtures. The concentrations of CHF_3 and CHF_2CF_3 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CHF_3)/k(HO + CHF_2CF_3) = (1.14\pm0.08)\times\exp[-(654\pm44)/T]$ is placed on an absolute basis by using a rate coefficient of $k(HO + CHF_2CF_3) = 9.46\times10^{19}\ T^2\ \exp(-1126/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) The absolute rate coefficients of Ernst *et al.*[7] and Jeong and Kaufman[8,9] were fitted to the three-parameter equation, $k=CT^2\ \exp(-D/T)$, resulting in $k=1.49\times10^{-18}\ T^2\exp(-1887/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 387–1445 K. The Arrhenius expression, $k=A\ \exp(-B/T)$, was centered at 300 K and was derived from the three parameter equation with $A=C\ e^2\ T^2$ and $B=D+2T$.

(d) Derived from the absolute rate coefficient data of Ernst *et al.*[7] and Jeong and Kaufman,[8,9] using the three parameter equation $k=CT^2\ \exp(-D/T)$.

(e) Derived from the 296 K rate coefficient of Howard and Evenson,[10] the 387 and 410 K rate coefficients of Jeong and Kaufman,[8,9] and the absolute and relative rate coefficients of Schmoltner *et al.*,[1] Kurylo *et al.* (unpublished data, 1994), and Hsu and DeMore.[2]

Preferred Values

$k=2.7\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=6.0\times10^{-13}\ \exp(-2295/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.
$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The absolute rate coefficient study of Schmoltner *et al.*[1] is the only published temperature-dependent study carried out at temperatures $\leqslant 298$ K. The rate coefficients derived from the relative rate study of Hsu and DeMore[2] are ~10–20% lower than the absolute rate coefficients of Schmoltner *et al.*[1] over the temperature range common to both studies (298–374 K), with the disagreement increasing with decreasing temperature. The rate coefficients measured at ~298 K by Howard and Evenson,[10] Nip *et al.*,[11] and Clyne and Holt[12] are highly uncertain, due to the low rate coefficient (note, for example, the reported invariance of the rate coefficient over the range 296–430 K from the study of Clyne and Holt[12]). The absolute rate coefficients of Ernst *et al.*,[7] Jeong and Kaufman,[8,9] and Schmoltner *et al.*[1] have been fitted to the three parameter equation $k=CT^2\ \exp(-D/T)$, resulting in $k=1.29\times10^{-18}\ T^2\exp(-1765/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 252–1445 K. At 298 K, this equation yields $k=3.07\times10^{-16}$ cm^3 molecule^{-1} s^{-1}, in agreement within the error limits with the room temperature rate coefficients of Howard and Evenson[10] and Nip *et al.*[11]

The relative rate coefficients of Hsu and DeMore[2] are uniformly 21% lower than those predicted from the three parameter expression over the temperature range 240–300 K. Accordingly, the value of C in the three parameter equation has been decreased by 10% to 1.15×10^{-18} cm^3 molecule^{-1} s^{-1}. The preferred Arrhenius expression, $k=A\times\exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A=C\ e^2\ T^2$ and $B=D+2T$.

References

[1] A. M. Schmoltner, R. K. Talukdar, R. F. Warren, A. Mellouki, L. Goldfarb, T. Gierczak, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **97**, 8976 (1993).
[2] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 1**, 1 (1989).
[5] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[6] NASA Evaluation No. 11, 1994 (see references in Introduction).
[7] J. Ernst, H. Gg. Wagner, and R. Zellner, Ber. Bunsenges. Phys. Chem. **82**, 409 (1978).
[8] K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).
[9] K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. **88**, 1222 (1984).
[10] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[11] W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. **83**, 2440 (1979).
[12] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).

$HO + CF_4 \rightarrow HOF + CF_3$

$\Delta H°=328$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<4\times10^{-16}$	296±2	Howard and Evenson, 1976[1]	(a)
$<1\times10^{-15}$	293	Clyne and Holt, 1979[2]	(b)
$<2\times10^{-18}$	~298	Ravishankara *et al.*, 1993[3]	(c)
Reviews and Evaluations			
$<2\times10^{-18}$	298	Atkinson, 1994[4]	(d)

Comments

(a) Discharge flow system with LMR detection of HO radicals.

(b) Discharge flow system with resonance fluorescence detection of HO radicals.

(c) Not explicitly reported, but expected to be a pulsed photolysis system with LIF detection of HO radicals as carried out by Schmoltner *et al.*[5] for HO radical reaction rate coefficient measurements with related hydrofluorocarbons.

(d) Based on the upper limit reported by Ravishankara *et al.*,[3] which is consistent with the higher upper limits of Howard and Evenson[1] and Clyne and Holt.[2]

Preferred Values

$k < 2 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

The preferred value is the upper limit to the rate coefficient reported by Ravishankara *et al.*[3]

References

[1] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[2] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 569 (1979).
[3] A. R. Ravishankara, S. Solomon, A. A. Turnipseed, and R. F. Warren, Science **259**, 194 (1993).
[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[5] A. M. Schmoltner, R. K. Talukdar, R. F. Warren, A. Mellouki, L. Goldfarb, T. Gierczak, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **97**, 8976 (1993).

$HO + CH_3CH_2F$(HFC-161) $\rightarrow H_2O + CH_3CHF$ (1)
$\rightarrow H_2O + CH_2CH_2F$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.69 \times 10^{-12} \exp[-(750 \pm 100)/T]$	243–373	Schmoltner *et al.*, 1993[1]	(a)
$(2.17 \pm 0.29) \times 10^{-13}$	298		
Relative Rate Coefficients			
$1.76 \times 10^{-17}\, T^2 \exp[-(657 \pm 36)/T]$	285–364	Hsu and DeMore, 1995[2]	(b)
1.69×10^{-13}	298		
Reviews and Evaluations			
2.3×10^{-13}	298	IUPAC, 1992[3]	(c)
$7.0 \times 10^{-12} \exp(-1100/T)$	243–373	NASA, 1994[4]	(d)

Comments

(a) Pulsed photolysis system with LIF detection of HO radicals.

(b) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or of H_2O-O_3 mixtures in the UV in H_2O (or H_2O-O_3)-CH_3CH_2F-C_2H_6-O_2-N_2 mixtures. The concentrations of CH_3CH_2F and C_2H_6 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3CH_2F)/k(HO + C_2H_6) = (1.16 \pm 0.13) \exp[-(158 \pm 36)/T]$ is placed on an absolute basis using a rate coefficient of $k(HO + C_2H_6) = 1.52 \times 10^{-17}\, T^2 \times \exp(-499/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Based on the rate coefficient of Nip *et al.*[5]

(d) Based on the rate coefficients of Nip *et al.*,[5] Schmoltner *et al.*,[1] and Hsu and DeMore.[2]

Preferred Values

$k = 2.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.4 \times 10^{-12} \exp(-740/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.
$k_1/k = 0.85$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 300$ K.
$\Delta k_1/k = \pm 0.15$ at 298 K.

Comments on Preferred Values

The absolute room temperature rate coefficients of Nip *et al.*[5] and Schmoltner *et al.*[1] are in excellent agreement, but are significantly higher than the relative rate coefficient of Hsu and DeMore.[2] The relative rate coefficients of Hsu and DeMore[2] are ~10% higher than the absolute rate coefficients of Schmoltner *et al.*[1] at 364 K, but ~25% lower at 285 K, with a significantly higher temperature dependence. The absolute rate coefficients of Nip *et al.*[5] and Schmoltner *et al.*[1] and the relative rate coefficients of Hsu and DeMore[1] have been fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 4.72 \times 10^{-18}\, T^2 \exp(-213/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 243–373 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter expression with $A = C\, e^2\, T^2$ and $B = D + 2T$.

The branching ratio is taken from the product study of Singleton *et al.*[6]

References

[1] A. M. Schmoltner, R. K. Talukdar, R. F. Warren, A. Mellouki, L. Goldfarb, B. Gierczak, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **97**, 8976 (1993).

[2] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] NASA, Evaluation No. 11, 1994 (see references in Introduction).

[5] W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. **83**, 2440 (1979).

[6] D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, J. Phys. Chem. **84**, 2339 (1980).

$HO + CH_3CHF_2(HFC\text{-}152a) \rightarrow H_2O + CH_2CHF_2$ (1)
$\rightarrow H_2O + CH_3CF_2$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.9\times10^{-12}\exp[-(1370\pm260)/T]$	295–388	Nielsen, 1991[1]	(a)
$(4.7\pm1.1)\times10^{-14}$	295		
Relative Rate Coefficients			
$(4.03\pm0.69)\times10^{-14}$	298±2	DeMore, 1992[2]	(b)
$3.44\times10^{-18}\,T^2\exp[\ \ (690\pm57)/T]$	298–358	Hsu and DeMore, 1995[3]	(c)
3.07×10^{-14}	298		
$(3.22\pm0.34)\times10^{-14}$	298±2	DeMore, 1992[2]	(d)
$6.18\times10^{-20}\,T^{2.58}\exp[-(483\pm67)/T]$	298–358	Hsu and DeMore, 1995[3]	(d)
2.96×10^{-14}	298		
Reviews and Evaluations			
$1.0\times10^{-12}\exp(-990/T)$	240–300	IUPAC, 1992[4]	(e)
$1.98\times10^{-18}\,T^2\exp(-460/T)$	212–423	Atkinson, 1994[5]	(f)
$2.4\times10^{-12}\exp(-1260/T)$	298–358	NASA, 1994[6]	(g)

Comments

(a) Pulsed radiolysis system with resonance absorption detection of HO radicals.

(b) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm in H_2O-CH_3CHF_2-C_2H_6-N_2-O_2 mixtures. The concentrations of CH_3CHF_2 and C_2H_6 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3CHF_2)/k(HO + C_2H_6)=0.161\pm0.028$ is placed on an absolute basis by use of a rate coefficient of $k(HO + C_2H_6)=2.5\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or H_2O-O_3)-CH_3CHF_2-CH_3CCl_3-O_2-N_2 mixtures. The concentrations of CH_3CHF_2 and CH_3CCl_3 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3CHF_2)/k(HO + CH_3CCl_3)=(1.53\pm0.28)\times\exp[(220\pm57)/T]$ is placed on an absolute basis by use of a rate coefficient of $k(HO + CH_3CCl_3)=2.25\times10^{-18}\,T^2\exp(-910/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in H_2O (or O_3-H_2O)-CH_3CHF_2-CH_4-N_2-O_2 mixtures. The concentrations of CH_3CHF_2 and CH_4 were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(HO + CH_3CHF_2)/k(HO + CH_4)=5.2\pm0.54$[2] and $k(HO + CH_3CHF_2)/k(HO + CH_4)=(0.64\pm0.13)\exp[(599\pm67)/T]$[3] are placed on an absolute basis by use of a rate coefficient of $k(HO + CH_4)=9.65\times10^{-20}\,T^{2.58}\exp(-1082/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) Derived from the rate coefficients of Howard and Evenson,[7] Handwerk and Zellner,[8] Nip *et al.*,[9] Liu *et al.*,[10] and Gierczak *et al.*[11]

(f) Derived from the rate coefficients of Howard and Evenson,[7] Handwerk and Zellner,[8] Nip *et al.*,[9] Liu *et al.*,[10] and Gierczak *et al.*[11] using the three parameter equation $k=CT^2\exp(-D/T)$.

(g) Derived from the room temperature rate coefficient data of Howard and Evenson,[7] Handwerk and Zellner,[8] Nip *et al.*,[9] Liu *et al.*,[10] Gierczak *et al.*,[11] Nielsen,[1] and Hsu and DeMore[3] and the temperature dependence measured by Hsu and DeMore.[3]

Preferred Values

$k=3.6\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.0\times10^{-12}\exp(-990/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k = ^{+0.10}_{-0.20}$ at 298 K.

$\Delta(E/R) = ^{+200}_{-400}$ K.

Comments on Preferred Values

The rate coefficients of Nielsen[1] over the temperature range 295–388 K are consistently higher than the absolute rate coefficients of Howard and Evenson,[7] Handwerk and Zellner,[8] Nip *et al.*,[9] Liu *et al.*,[10] Brown *et al.*,[12] and Gierczak *et al.*,[11] all of which are in reasonably good agreement at room temperature. The 298 K relative rate coefficients of DeMore[2] are also in good agreement with the room temperature absolute rate coefficients of Howard and Evenson,[7] Handwerk and Zellner,[8] Nip *et al.*,[9] Liu *et al.*,[10] Brown *et al.*,[12] and Gierczak *et al.*[11] However, the more recent rate coefficients measured by Hsu and DeMore[3] relative to the rate coefficients for the HO radical reactions with CH_4 and CH_3CCl_3 (which are in good agreement) are ~10% lower than the least-squares average of the absolute rate coefficients of Howard and Evenson,[7] Handwerk and Zellner,[8] Nip *et al.*,[9] Liu *et al.*,[10] and Gierczak *et al.*[11] at 358 K, and ~15–20% lower at 298 K. While this discrepancy is relatively minor, and within the combined overall uncertainties, the temperature dependence obtained by Hsu and DeMore[3] is higher than that derived from the absolute rate coefficients.[7–11]

The temperature dependent studies of Liu *et al.*,[10] Brown *et al.*,[12] and Gierczak *et al.*[11] also agree well. As in previous evaluations[4–6] the data of Clyne and Holt[13] are omitted. The absolute rate coefficients measured by Brown *et al.*[12] are subject to large uncertainties, as evidenced by the high standard deviations cited at several temperatures, especially at 220 K and 303 K. Because of this and the observations that in general the rate coefficients of Brown *et al.*[12] are significantly higher than those of other recent studies (see the data sheets for other OH + HCFC and HFC reactions in this evaluation), these data of Brown *et al.*[12] were not used in the evaluation of the rate coefficient for this reaction.

The absolute rate coefficient data of Howard and Evenson,[7] Handwerk and Zellner,[8] Nip *et al.*,[9] Liu *et al.*,[10] and Gierczak *et al.*[11] have been fitted to the three parameter equation $k=CT^2\exp(-D/T)$, resulting in $k=1.98\times10^{-18}\times T^2\exp(-460/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 212–423 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$, is centered at 265 K, and is derived from the three parameter equation with $A=C\,e^2\,T^2$ and $B=D+2T$. The uncertainties on the preferred values are such that they take into account the lower rate coefficients obtained by Hsu and DeMore,[3] which extrapolate to a rate coefficient at 240 K which is 30% lower than that calculated from the preferred Arrhenius expression.

References

[1] O. J. Nielsen, Chem. Phys. Lett. **187**, 286 (1991).
[2] W. B. DeMore, *Optical Methods in Atmospheric Chemistry* [Proc. SPIE **1715**, 72 (1992)].
[3] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).
[5] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, (1994).
[6] NASA Evaluation No. 11, 1994 (see references in Introduction).
[7] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 4303 (1976).
[8] V. Handwerk and R. Zellner, Ber. Bunsenges. Phys. Chem. **82**, 1161 (1978).
[9] W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. **83**, 2440 (1979).
[10] R. Liu, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. **94**, 3247 (1990).
[11] T. Gierczak, R. Talukdar, G. L. Vaghjiani, E. R. Lovejoy, and A. R. Ravishankara, J. Geophys. Res. **96**, 5001 (1991).
[12] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).
[13] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).

HO + CH_3CF_3(HFC-143a) → H_2O + CH_2CF_3

$\Delta H^\circ = -49.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$4.15\times10^{-20}\,T^{2.58}\exp[-(1305\pm90)/T]$	298–403	Hsu and DeMore, 1995[1]	(a)
1.27×10^{-15}	298		
$2.04\times10^{-18}\,T^2\exp[-(1496\pm21)/T]$	298–383	Hsu and DeMore, 1995[1]	(a)
1.20×10^{-15}	298		
Reviews and Evaluations			
$1.05\times10^{-12}\exp(-1990/T)$	240–300	IUPAC, 1992[2]	(b)
$2.02\times10^{-18}\,T^2\exp(-1459/T)$	223–374	Atkinson, 1994[3]	(c)
$1.6\times10^{-12}\exp(-2100/T)$	251–374	NASA, 1994[4]	(d)

Comments

(a) Relative rate method. HO radicals generated by the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or O_3-H_2O)-CH_3CF_3-CH_4 (or CHF_2CF_3)-O_2-N_2 mixtures. The concentrations of CH_3CF_3 and CH_4 (or CHF_2CF_3) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(HO + CH_3CF_3)/k(HO + CH_4) = (0.43\pm0.12) \times \exp[-(223\pm90)/T]$ and $k(HO + CH_3CF_3)/k(HO + CHF_2CF_3) = (2.16\pm0.14)\ \exp[-(370\pm21)/T]$ were placed on an absolute basis by use of rate coefficients of $k(HO + CH_4) = 9.65\times10^{-20}\ T^{2.58}\ \exp(-1082/T)$ $cm^3\ molecule^{-1}\ s^{-1}$ (this evaluation) and $k(HO + CHF_2CF_3) = 9.46\times10^{-19}\ T^2\ \exp(-1126/T)$ $cm^3\ molecule^{-1}\ s^{-1}$ (this evaluation).

(b) Based on the absolute rate coefficients of Martin and Paraskevopoulos[5] and Talukdar *et al.*[6]

(c) Derived from the absolute rate coefficients of Martin and Paraskevopoulos[5] and Talukdar *et al.*,[6] using the three parameter equation $k = CT^2\ \exp(-D/T)$.

(d) Based on the absolute room temperature rate coefficients of Martin and Paraskevopoulos[5] and the absolute rate coefficients of Talukdar *et al.*[6] at temperatures >251 K.

Preferred Values

$k = 1.3\times10^{-15}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k = 1.05\times10^{-12}\ \exp(-1990/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The room temperature absolute rate coefficients of Martin and Paraskevopoulos[5] and Talukdar *et al.*[6] are in reasonable agreement. The rate coefficients of Clyne and Holt[7] are not used in the evaluation because their rate coefficients at 333 K and 378 K are significantly higher than those of Talukdar *et al.*,[6] and have large associated cited uncertainties. The absolute rate coefficients of Martin and Paraskevopoulos[5] and Talukdar *et al.*[6] have been fitted to the three parameter equation $k = CT^2\ \exp(-D/T)$, resulting in $k = 2.02\times10^{-18}\ T^2 \times \exp(-1459/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 223–374 K. The preferred Arrhenius expression $k = A \times \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = C\ e^2\ T^2$ and $B = D + 2T$. The preferred values are identical to our previous evaluation, IUPAC, 1992.[2] The rate coefficients of Hsu and DeMore,[1] relative to the rate coefficients for the reactions of the HO radical with CH_4 and CHF_2CF_3, are in excellent agreement with each other, and the extrapolated rate coefficients of Hsu and DeMore[1] are 7–13% lower than the preferred values over the temperature range 240–300 K.

References

[1] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] R. Atkinson J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

[5] J.-P. Martin and G. Paraskevopoulos, Can. J. Chem. **61**, 861 (1983).

[6] R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **95**, 5815 (1991).

[7] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).

$HO + CH_2FCH_2F$ (HFC-152) → $H_2O + CH_2FCHF$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.12\pm0.12)\times10^{-13}$	298	Martin and Paraskevopoulos, 1983[1]	(a)
Reviews and Evaluations			
$1.7\times10^{-11}\ \exp(-1500/T)$	200–300	NASA, 1994[2]	(b)

Comments

(a) Flash photolysis system with resonance absorption detection of HO radicals.

(b) The 298 K rate coefficient was based on the rate coefficient of Martin and Paraskevopoulos.[1] The temperature dependence was estimated.

Preferred Values

$k = 1.1\times10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the absolute rate coefficient of Martin and Paraskevopoulos.[1]

References

[1] J.-P. Martin and G. Paraskevopoulos, Can. J. Chem. **61**, 861 (1983).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

HO + CH_2FCHF_2(HFC-143) → H_2O + CH_2FCF_2 (1)

→ H_2O + $CHFCHF_2$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
4.97×10^{-18} T^2 exp($-1012/T$)	278–323	Barry *et al.*, 1995[1]	(a)
$(1.49\pm0.05)\times10^{-14}$	298±2		
Reviews and Evaluations			
1.8×10^{-14}	298	IUPAC, 1992[2]	(b)
4.0×10^{-12} exp($-1650/T$)	278–323	NASA, 1994[3]	(c)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of O_3 in the presence of water vapor at ~250 nm at atmospheric pressure of air. Irradiations of O_3-H_2O-CH_2FCHF_2-CH_3CCl_3-air mixtures were carried out and the concentrations of CH_2FCHF_2 and CH_3CCl_3 measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of $k(HO+CH_2FCHF_2)/k(HO+CH_3CCl_3)=2.21\ \exp(-102/T)$ is placed on an absolute basis by use of a rate coefficient of $k(HO+CH_3CCl_3)=2.25\times10^{-18}T^2\times\exp(-910/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Based on the room temperature absolute rate coefficient of Martin and Paraskevopoulos.[4]

(c) Based on the relative rate coefficients of Barry *et al.*[1]

Preferred Values

$k=1.5\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=3.3\times10^{-12}$ exp($-1610/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The preferred rate coefficients are derived from the relative rate study of Barry *et al.*[1] The preferred Arrhenius expression, $k=A\exp(-B/T)$, is derived from the three parameter expression cited in the table, of $k=4.97\times10^{18}\ T^2\times\exp(-1012/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 278–323 K, and is centered at 300 K with $A=C\,e^2\,T^2$ and $B=D+2T$. The 298 K rate coefficient of Martin and Paraskevopoulos[4] is in reasonable agreement with this recommendation.

References

[1] J. Barry, H. Sidebottom, J. Treacy, and J. Franklin, Int. J. Chem. Kinet. **27**, 27 (1995).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] J.-P. Martin and G. Paraskevopoulos, Can. J. Chem. **61**, 861 (1983).

$HO + CH_2FCF_3$ (HFC-134a) → $H_2O + CHFCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.38\pm0.22)\times10^{-15}$	270	Zhang, Huie, and Kurylo, 1992[1]	(a)
$1.03\times10^{-12}\exp[-(1588\pm52)/T]$	298–460	Orkin and Khamaganov, 1993[2]	(b)
$(5.0\pm0.44)\times10^{-15}$	298		
$9.9\times10^{-13}\exp[-(1640\pm150)/T]$	255–424	Leu and Lee, 1994[3]	(c)
$(3.9\pm0.6)\times10^{-15}$	298		
Relative Rate Coefficients			
$4.31\times10^{-20}\,T^{2.58}\exp[-(1000\pm115)/T]$	298–358	DeMore, 1993[4]	(d,e)
3.64×10^{-15}	298		
$1.84\times10^{-18}\,T^2\exp[-(1129\pm44)/T]$	298–358	DeMore, 1993[4]	(d,f)
3.70×10^{-15}	298		
$1.97\times10^{-18}\,T^2\exp[-(1138\pm79)/T]$	298–358	DeMore, 1993[4]	(d,g)
3.80×10^{-15}	298		
$(3.90\pm0.48)\times10^{-15}$	298±2	Barry *et al.*, 1995[5]	(h)
$(4.19\pm0.19)\times10^{-15}$	298±2	Barry *et al.*, 1995[5]	(i)
Reviews and Evaluations			
$8.4\times10^{-13}\exp(-1535/T)$	240–300	IUPAC, 1992[6]	(j)
$1.61\times10^{-18}\,T^2\exp(-1005/T)$	223–450	Atkinson, 1994[7]	(k)
$1.5\times10^{-12}\exp(-1750/T)$	243–450	NASA, 1994[8]	(l)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO radicals.

(b) Discharge flow system with EPR detection of HO radicals.

(c) Discharge flow system with resonance fluorescence detection of HO radicals.

(d) Relative rate method. HO radicals were generated by the photolysis of O_3-H_2O-O_2-Ar mixtures at 254 nm. The CH_2FCF_3 and CH_4, CH_3CCl_3, or CHF_2CF_3 concentrations were monitored during the experiments by FTIR absorption spectroscopy. The measured rate coefficient ratios of $k(HO + CH_4)/k(HO + CH_2FCF_3) = (2.24 \pm 0.78)\exp[-(82 \pm 115)/T]$, $k(HO + CH_3CCl_3)/k(HO + CH_2FCF_3) = (1.22 \pm 0.17)\times\exp[(219\pm44)/T]$ and $k(HO + CHF_2CF_3)/k(HO + CH_2FCF_3) = (0.48\pm0.12)\exp[(12\pm79)/T]$ are placed on an absolute basis by use of rate coefficients of $k(HO + CH_4) = 9.65\times10^{-20}\ T^{2.58}\exp(-1082/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation), $k(HO + CH_3CCl_3) = 2.25\times10^{-18}\ T^2\exp(-910/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation) and $k(HO + CHF_2CF_3) = 9.46\times10^{-19}\times T^2\exp(-1126/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) Relative to $k(HO + CH_4)$.

(f) Relative to $k(HO + CH_3CCl_3)$.

(g) Relative to $k(HO + CHF_2CF_3)$.

(h) Relative rate method. HO radicals were generated by the photolysis of O_3 at ~250 nm in the presence of water vapor at atmospheric pressure of air. Irradiations of O_3-H_2O-CH_2FCF_3-CH_3CCl_3-air mixtures were carried out at 298±2 K and the concentrations of CH_2FCF_3 and CH_3CCl_3 measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_2FCF_3)/k(HO + CH_3CCl_3) = 0.41\pm0.05$ is placed on an absolute basis by using a rate coefficient of $k(HO + CH_3CCl_3) = 9.5\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K (this evaluation).

(i) Relative rate method. HO radicals were generated by the photolysis of O_3 in the presence of water vapor. Irradiations of O_3-H_2O-CH_2FCF_3-CH_2FCHF_2-air mixtures were carried out at 298±2 K and the concentrations of CH_2FCF_3 and CH_2FCHF_2 measured by GC and FTIR spectroscopy. The measured rate coefficient ratio $k(HO + CH_2FCHF_2)/k(HO + CH_2FCF_3) = 3.58\pm0.16$ is placed on an absolute basis by using a rate coefficient of $k(HO + CH_2FCHF_2) = 1.5\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K (this evaluation).

(j) Derived from the absolute rate coefficients of Martin and Paraskevopoulos,[9] Liu *et al.*,[10] and Gierczak *et al.*[11]

(k) Derived from the absolute rate coefficients of Martin and Paraskevopoulos,[9] Liu *et al.*,[10] and Gierczak *et al.*,[11] using the three parameter equation $k = CT^2\times\exp(-D/T)$.

(l) Derived from the absolute rate coefficients of Martin and Paraskevopoulos,[9] Liu *et al.*,[10] Gierczak *et al.*,[11] (for $T \geq 243$ K), Zhang *et al.*,[1] and Leu and Lee,[3] and the relative rate coefficients of DeMore.[4]

Preferred Values

$k = 4.2\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=7.3\times10^{-13}\exp(-1540/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The absolute rate coefficient of Zhang *et al.*[1] at 270 K is in good agreement with those of Liu *et al.*[10] and Gierczak *et al.*[11] at 270–273 K, and the absolute rate coefficients of Orkin and Khamaganov[2] are in agreement with those of Liu *et al.*[10] and Gierczak *et al.*[11] However, the relative rate coefficients of DeMore[4] and Barry *et al.*[5] at 298 K are lower than those of Martin and Paraskevopoulos,[9] Liu *et al.*,[10] Gierczak *et al.*,[11] and Orkin and Khamaganov,[2] by up to 30%. The absolute rate coefficients of Gierczak *et al.*[11] are slightly or significantly lower than those of Martin and Paraskevopoulos,[9] Jeong *et al.*,[12] Liu *et al.*,[10] (especially at 350–400 K), Brown *et al.*,[13] and Orkin and Khamaganov.[2] The absolute rate coefficients of Leu and Lee[3] are in excellent agreement with the relative rate coefficients of DeMore[4] and Barry *et al.*,[5] and are ~10% lower than the absolute rate coefficients of Gierczak *et al.*[11]

The absolute rate coefficients of Gierczak *et al.*[11] (243–450 K), Zhang *et al.*[1] (at 270 K), and Leu and Lee[3] and the 298 K relative rate coefficients of DeMore[4] and Barry *et al.*[5] have been fitted to the three parameter equation $k=CT^2\times\exp(-D/T)$, resulting in $k=1.40\times10^{-18}\,T^2\exp(-1008/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 243–450 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$, is centered at 265 K and is derived from the three-parameter equation with $A=C\,e^2\,T^2$ and $B=D+2T$.

References

[1] Z. Zhang, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. **96**, 1533 (1992).

[2] V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 157 (1993).

[3] G.-H. Leu and Y.-P. Lee, J. Chin. Chem. Soc. **41**, 645 (1994).

[4] W. B. DeMore, Geophys. Res. Lett. **20**, 1359 (1993).

[5] J. Barry, H. Sidebottom, J. Treacy, and J. Franklin, Int. J. Chem. Kinet. **27**, 27 (1995).

[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

[7] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994)

[8] NASA Evaluation No. 11, 1994 (see references in Introduction).

[9] J.-P. Martin and G. Paraskevopoulos, Can. J. Chem. **61**, 861 (1983).

[10] R. Liu, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. **94**, 3247 (1990).

[11] T. Gierczak, R. Talukdar, G. L. Vaghjiani, E. R. Lovejoy, and A. R. Ravishankara, J. Geophys. Res. **96**, 5001 (1991).

[12] K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. **88**, 1222 (1984).

[13] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

$HO + CHF_2CHF_2(HFC\text{-}134) \rightarrow H_2O + CF_2CHF_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$2.68\times10^{-18}\,T^2\exp[-(1122\pm37)/T]$	298–358	DeMore, 1993[1]	(a)
5.51×10^{-15}	298		
$1.65\times10^{-18}\,T^2\exp[-(928\pm25)/T]$	298–358	DeMore, 1993[1]	(b)
6.46×10^{-15}	298		
$1.97\times10^{-18}\,T^2\exp[-(1017\pm77)/T]$	298–358	DeMore, 1993[1]	(c)
5.76×10^{-15}	298		
Reviews and Evaluations			
5.7×10^{-15}	298	IUPAC, 1992[2]	(d)
$1.6\times10^{-12}\exp(-1680/T)$	298–358	NASA, 1994[3]	(e)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of O_3-H_2O-O_2-Ar mixtures at 254 nm. The concentrations of CHF_2CHF_2 and CH_3CCl_3 were measured during the experiments by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3CCl_3)/k(HO + CHF_2CHF_2)=(0.84\pm0.10)\exp[(212\pm37)/T]$ is placed on an absolute basis by use of a rate coefficient of $k(HO + CH_3CCl_3)=2.25\times10^{-18}\,T^2\exp(-910/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Relative rate method. HO radicals were generated by the photolysis of O_3-H_2O-O_2-Ar mixtures at 254 nm. The concentrations of CHF_2CHF_2 and CH_2FCF_3 were measured during the irradiations by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(HO+CH_2FCF_3)/(k(HO+CHF_2CHF_2)=(0.85\pm0.07)\times\exp[-(80\pm25)/T]$ is placed on an absolute basis by use of a rate coefficient of $k(HO + CH_2FCF_3)=1.40\times10^{-18}\,T^2\exp(-1008/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Relative rate method. HO radicals were generated by photolysis of H_2O-O_3 mixtures at 254 nm. The concentrations of CHF_2CHF_2 and CHF_2CF_3 were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(HO + CHF_2CF_3)/k(HO + CHF_2CHF_2) = (0.48 \pm 0.11) \exp[-(109 \pm 77)/T]$ is placed on an absolute basis by use of a rate coefficient of $k(HO + CHF_2CF_3) = 9.46 \times 10^{-19} T^2 \exp(-1120/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Derived from the 298 K rate coefficient of Clyne and Holt.[4]

(e) Derived from the relative rate coefficients of DeMore.[1]

Preferred Values

$k = 5.9 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.4 \times 10^{-12} \exp(-1630/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are based on the relative rate coefficients of DeMore.[1] The 298 K rate coefficients and the temperature dependencies from the three sets of measurements[1] (relative to the reactions of the HO radical with CH_3CCl_3, CH_2FCF_3, and CHF_2CF_3), which are in good agreement, have been averaged and the *A*-factor calculated from the 298 K rate coefficient and the temperature dependence. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three-parameter expression with $A = C e^2 T^2$ and $B = D + 2T$. The 298 K preferred rate coefficient and the temperature dependence are in good agreement with the absolute rate coefficient data of Clyne and Holt.[4]

References

[1] W. B. DeMore, Geophys. Res. Lett. **20**, 1359 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).

$HO + CHF_2CF_3$ (HFC-125) $\rightarrow H_2O + CF_2CF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.59 \pm 0.21) \times 10^{-15}$	298	DeMore, 1992[1]	(a,b)
$(2.10 \pm 0.15) \times 10^{-15}$	298	DeMore, 1992[1]	(a,c)
$6.7 \times 10^{-19} T^2 \exp[-(996 \pm 79)/T]$	298–358	DeMore, 1993[2]	(a,d)
2.10×10^{-15}	298		
Reviews and Evaluations			
$4.9 \times 10^{-13} \exp(-1655/T)$	240–300	IUPAC, 1992[3]	(e)
$9.46 \times 10^{-19} T^2 \exp(-1126/T)$	220–364	Atkinson, 1994[4]	(f)
$5.6 \times 10^{-13} \exp(-1700/T)$	220–364	NASA, 1994[5]	(g)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of O_3 in the presence of water vapor at 254 nm. Irradiations of O_3-H_2O-CHF_2CF_3-reference organic-O_2-N_2 (or Ar) mixtures were carried out, and the concentrations of CHF_2CF_3 and the reference organic measured by FTIR absorption spectroscopy.

(b) Relative to $k(HO + CH_4)$, and the measured rate coefficient ratio $k(HO + CH_4)/k(HO + CHF_2CF_3) = 3.9 \pm 0.50$ is placed on an absolute basis by use of a rate coefficient of $k(HO + CH_4) = 6.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K (this evaluation).

(c) Relative to $k(HO + CH_2FCF_3)$, and the measured rate coefficient ratio $k(HO + CH_2FCF_3)/k(HO + CHF_2CF_3) = 2.0 \pm 0.14$ is placed on an absolute basis by use of a rate coefficient of $k(HO + CH_2FCF_3) = 4.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K (this evaluation).

(d) Relative to $k(HO + CH_2FCF_3)$, and the measured rate coefficient ratio $k(HO + CHF_2CF_3)/k(HO + CH_2FCF_3) = (0.48 \pm 0.12) \exp[(12 \pm 79)/T]$ is placed on an absolute basis by use of a rate coefficient of $k(HO + CH_2FCF_3) = 1.40 \times 10^{-18} T^2 \exp(-1008/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation). Rate coefficients were also measured relative to $k(HO + CHF_2CHF_2)$ but, because these data were used to evaluate the rate coefficient for the reaction of the HO radical with CHF_2CHF_2 (see previous data sheet), they are not used in this data sheet.

(e) Derived from the absolute rate coefficients of Martin and Paraskevopoulos[6] and Talukdar *et al.*[7]

(f) Derived from the absolute rate coefficients of Martin and Paraskevopoulos[6] and Talukdar *et al.*,[7] using the three parameter equation $k=CT^2 \exp(-D/T)$.

(g) Derived from the absolute rate coefficients of Martin and Paraskevopoulos[6] and Talukdar *et al.*[7] and the room temperature relative rate coefficient of DeMore.[2]

Preferred Values

$k=1.9\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=4.9\times10^{-13} \exp(-1655/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

At room temperature, the measured rate coefficients[1,2,6-9] cover a range of a factor of ~3, with the rate coefficients of Talukdar *et al.*[7] and DeMore[1,2] being the lowest. Combined with the temperature dependence observed by Talukdar *et al.*[7] being the highest, this suggests the presence of reactive impurities in the CHF_2CF_3 samples used in the studies of Clyne and Holt[8] and Brown *et al.*[9] The preferred rate coefficient is derived from the absolute rate coefficients of Martin and Paraskevopoulos[6] and Talukdar *et al.*[7]

These rate coefficient data[6,7] were fitted to the three parameter equation $k=CT^2 \exp(-D/T)$, resulting in $k=9.46\times10^{-19}\ T^2 \exp(-1126/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–364 K. The preferred Arrhenius expression, $k=A \exp(-B/T)$, was centered at 265 K and is derived from the three parameter equation with $A=C\,e^2\,T^2$ and $B=D+2T$. The preferred values are identical with those of our previous evaluation, IUPAC, 1992.[3] The relative rate coefficients of DeMore[1,2] are in good agreement with this recommendation.

References

[1] W. B. DeMore, *Optical Methods in Atmospheric Chemistry* [Proc. SPIE **1715**, 72 (1992)].
[2] W. B. DeMore, Geophys. Res. Lett. **20**, 1359 (1993).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[5] NASA Evaluation No. 11, 1994 (see references in Introduction).
[6] J.-P. Martin and G. Paraskevopoulos, Can. J. Chem. **61**, 861 (1983).
[7] R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **95**, 5815 (1991).
[8] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).
[9] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

$HO + CHF_2CF_2CH_2F$ (HFC-245ca) $\rightarrow H_2O + CHF_2CF_2CHF$ (1)

$\rightarrow H_2O + CF_2CF_2CH_2F$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.87\times10^{-12} \exp[-(1661\pm170)/T]$	260-365	Zhang *et al.*, 1994[1]	(a)
$(1.09\pm0.03)\times10^{-14}$	298		
Relative Rate Coefficients			
$6.47\times10^{-20}\ T^{2.58} \exp[-(918\pm34)/T]$	286-364	Hsu and DeMore, 1995[2]	(b)
7.47×10^{-15}	298		
Reviews and Evaluations			
$2.4\times10^{-12} \exp(-1660/T)$	260-365	NASA, 1994[3]	(c)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO radicals.

(b) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or H_2O-O_3)-$CHF_2CF_2CH_2F$-CH_4-O_2-N_2 mixtures. The concentrations of $CHF_2CF_2CH_2F$ and CH_4 were measured by FTIR absorption spectroscopy. The measured rate coefficient of $k(HO + CHF_2CF_2CH_2F)/k(HO + CH_4) =(0.67\pm0.07) \exp[(164\pm34/T]$ is placed on an absolute basis by use of a rate coefficient of $k(HO + CH_4)=9.65\times10^{-20}\ T^{2.58} \exp(-1082/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Based on the absolute and relative rate coefficients of Zhang *et al.*[1] and Hsu and DeMore.[2]

Preferred Values

$k=7.2\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=2.1\times10^{-12}\exp(-1690/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The relative rate coefficients of Hsu and DeMore[2] are uniformly a factor of 1.5 lower than the absolute rate coefficients of Zhang *et al.*[1] over the temperature range common to both studies (286–364 K). This suggests the presence of reactive impurities or of secondary reactions in the study of Zhang *et al.*[1] The relative rate coefficients of Hsu and DeMore[2] are used to derive the preferred values. The preferred Arrhenius expression, $k=A\exp(-B/T)$, is centered at 300 K and is derived from the three parameter equation, $k=CT^n\exp(-D/T)$, cited in the table with $A=C\,e^n\,T^n$ and $B=D+nT$. The temperature dependence of the resultant Arrhenius expression is almost identical to that of Zhang *et al.*[1]

References

[1] Z. Zhang, S. Padmaja, R. D. Saini, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. **98**, 4312 (1994).
[2] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

HO + $CF_3CF_2CH_2F$ (HFC-236cb) → H_2O + CF_3CF_2CHF

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.6\times10^{-13}\exp[-(1107\pm202)/T]$	256–314	Garland *et al.*, 1993[1]	(a)
$(6.4\pm0.6)\times10^{-15}$	295		
Reviews and Evaluations			
$1.5\times10^{-12}\exp(-1750/T)$	~200–300	NASA, 1994[2]	(b)

Comments

(a) Laser photolysis system with LIF detection of HO radicals.

(b) Estimated by analogy with the reaction of the HO radical with CF_3CH_2F.

Preferred Values

$k=6\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is that calculated from the Arrhenius expression of Garland *et al.*[1] Because of the low *A* factor reported by Garland *et al.*,[1] no temperature dependence is recommended.

References

[1] N. L. Garland, L. J. Medhurst, and H. H. Nelson, J. Geophys. Res. **98**, 23107 (1993).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$HO + CF_3CHFCHF_2(HFC\text{-}236ea) \rightarrow H_2O + CF_3CFCHF_2$ (1)
$\rightarrow H_2O + CF_3CHFCF_2$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.0×10^{-13} exp[$-(1007\pm151)/T$]	251–311	Garland, Medhurst, and Nelson, 1993[1]	(a)
$(6.5\pm0.5)\times10^{-15}$	294		
1.05×10^{-12} exp[$-(1434\pm161)/T$]	260–365	Zhang *et al.*, 1994[2]	(b)
$(8.51\pm0.26)\times10^{-15}$	298		
Relative Rate Coefficients			
3.47×10^{-20} $T^{2.58}$ exp[$-(851\pm12)/T$]	298–380	Hsu and DeMore, 1995[3]	(c)
4.94×10^{-15}	298		
Reviews and Evaluations			
1.2×10^{-12} exp($-1550/T$)	251–365	NASA, 1994[4]	(d)

Comments

(a) Laser photolysis system with LIF detection of HO radicals.

(b) Flash photolysis system with resonance fluorescence detection of HO radicals.

(c) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV, in H_2O (or O_3-H_2O)-$CF_3CHFCHF_2$-CH_4-O_2-N_2 mixtures. The concentrations of $CF_3CHFCHF_2$ and CH_4 were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(HO + CF_3CHFCHF_2)/k(HO + CH_4) = (0.36\pm0.01)$ exp[$(231\pm12)/T$] is placed on an absolute basis by using a rate coefficient of $k(HO + CH_4) = 9.65\times10^{-20}$ $T^{2.58}$ exp($-1082/T$) cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Derived from the absolute rate coefficients of Garland *et al.*[1] and Zhang *et al.*[2] and the relative rate coefficients of Hsu and DeMore.[3]

Preferred Values

$k=4.8\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.1\times10^{-12}$ exp($-1620/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The three studies carried out to date[1-3] are not in good agreement, with the relative rate coefficients of Hsu and DeMore[3] being the lowest and exhibiting the highest temperature dependence. This observation may suggest the presence of reactive impurities in the two absolute rate studies.[1,2] Accordingly, the relative rate coefficients of Hsu and DeMore[3] are used to derive the preferred values. The preferred Arrhenius expression, $k=A$ exp($-B/T$), is centered at 300 K and is derived from the three parameter equation, $k=CT^n$ exp($-D/T$), of Hsu and DeMore[3] cited in the table with $A=C$ e^n T^n and $B=D+nT$.

References

[1] N. L. Garland, L. J. Medhurst, and H. H. Nelson, J. Geophys. Res. **98**, 23107 (1993).

[2] Z. Zhang, S. Padmaja, R. D. Saini, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. **98**, 4312 (1994).

[3] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

HO + $CF_3CH_2CF_3$(HFC-236fa) → H_2O + CF_3CHCF_3

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.0×10^{-14} exp[$-(906\pm151)/T$]	257–311	Garland, Medhurst, and Nelson, 1993[1]	(a)
9.6×10^{-16}	298		
Relative Rate Coefficients			
1.19×10^{-18} T^2 exp[$-(1706\pm109)/T$]	298–367	Hsu and DeMore, 1995[2]	(b)
3.71×10^{-16}	298		
Reviews and Evaluations			
7.1×10^{-13} exp($-2280/T$)		NASA, 1994[3]	(c)

Comments

(a) Laser photolysis system with LIF detection of HO radicals.

(b) Relative rate method. HO radicals were generated from the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or O_3-H_2O)-$CF_3CH_2CF_3$-CHF_2CF_3-O_2-N_2 mixtures. The concentrations of $CF_3CH_2CF_3$ and CHF_2CF_3 were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of k(HO + $CF_3CH_2CF_3$)/k(HO + CHF_2CF_3) =(1.26 ± 0.41) exp[$-(580\pm109)/T$] is placed on an absolute basis by using a rate coefficient of k(HO + CHF_2CF_3)=9.46×10^{-19} T^2 exp($-1126/T$) cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Based on the relative rate coefficients of Hsu and DeMore.[2]

Preferred Values

$k=3.5\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=7.9\times10^{-13}$ exp($-2305/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

$\Delta(E/R)=\pm400$ K.

Comments on Preferred Values

The relative rate coefficient of Hsu and DeMore[2] at 312 K is a factor of 2.4 lower than the absolute rate coefficient of Garland *et al.*[1] at 311 K (the only temperature common to both studies). Furthermore, the temperature dependence measured by Garland *et al.*[1] is significantly lower than that of Hsu and DeMore[2] (B=900 K[1] versus 2300 K[2]), suggesting the presence of reactive impurities in the $CF_3CH_2CF_3$ sample used by Garland *et al.*[1]

The preferred values are derived from the relative rate coefficients of Hsu and DeMore.[2] The preferred Arrhenius expression, $k=A$ exp($-B/T$), is centered at 300 K and is derived from the three parameter equation, $k=CT^2$ exp($-D/T$), cited in the table with $A=C$ e^2 T^2 and $B=D+2T$.

References

[1] N. L. Garland, L. J. Medhurst, and H. H. Nelson, J. Geophys. Res. **98**, 23107 (1993).
[2] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$HO + CF_3CHFCF_3(HFC\text{-}227ea) \rightarrow H_2O + CF_3CFCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.7\times10^{-13}\exp[-(1615\pm190)/T]$	294–369	Nelson, Zahniser, and Kolb, 1993[1]	(a)
$(1.65\pm0.28)\times10^{-15}$	295		
$3.8\times10^{-13}\exp[-(1596\pm77)/T]$	298–463	Zellner *et al.*, 1994[2]	(a)
$(1.8\pm0.2)\times10^{-15}$	298		
$3.63\times10^{-13}\exp[-(1613\pm135)/T]$	270–365	Zhang *et al.*, 1994[3]	(b)
$(1.62\pm0.03)\times10^{-15}$	298		
Relative Rate Coefficients			
$1.64\times10^{-20}\,T^{2.58}\exp[-(965\pm105)/T]$	296–398	Hsu and DeMore, 1995[4]	(c,d)
1.51×10^{-15}	296		
$7.85\times10^{-19}\,T^{2}\exp[-(1088\pm89)/T]$	298–367	Hsu and DeMore, 1995[4]	(c,e)
1.88×10^{-15}	298		
Reviews and Evaluations			
$5.0\times10^{-13}\exp(-1700/T)$	270–463	NASA, 1994[5]	(f)

Comments

(a) Discharge flow system with LIF detection of HO radicals.

(b) Flash photolysis system with resonance fluorescence detection of HO radicals.

(c) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or H_2O-O_3)-CF_3CHFCF_3-CH_4 (or CHF_2CF_3)-O_2-N_2 mixtures. The concentrations of CF_3CHFCF_3 and CH_4 (or CHF_2CF_3) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratios of $k(HO + CF_3CHFCF_3)/k(HO + CH_4) = (0.17\pm0.05)\times\exp[(117\pm105)/T]$ and $k(HO + CF_3CHFCF_3)/k(HO + CHF_2CF_3) = (0.83\pm0.22)\exp[(38\pm89)/T]$ are placed on an absolute basis by use of rate coefficients of $k(HO + CH_4) = 9.65\times10^{-20}\,T^{2.58}\exp(-1082/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation) and $k(HO + CHF_2CF_3) = 9.46\times10^{-19}\,T^2\exp(-1126/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Relative to $k(HO + CH_4)$.

(e) Relative to $k(HO + CHF_2CF_3)$.

(f) Derived from the rate coefficients of Nelson *et al.*,[1] Zellner *et al.*,[2] Zhang *et al.*,[3] Koch and Zetzsch (unpublished data, 1993), and Hsu and DeMore.[4]

Preferred Values

$k = 1.6\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.5\times10^{-13}\exp(-1675/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–463 K.

Reliability

$\Delta\log k = \pm0.2$ at 298 K.

$\Delta(E/R) = \pm300$ K.

Comments on Preferred Values

The preferred values are obtained from a least-squares analysis of the absolute rate coefficients of Nelson *et al.*,[1] Zellner *et al.*,[2] and Zhang *et al.*,[3] which are in good agreement and which also agree well with the relative rate coefficients of Hsu and DeMore.[4]

References

[1] D. D. Nelson, M. S. Zahniser, and C. E. Kolb, Geophys. Res. Lett. **20**, 197 (1993).

[2] R. Zellner, G. Bednarek, A. Hoffmann, J. P. Kohlmann, V. Mörs, and H. Saathoff, Ber. Bunsenges. Phys. Chem. **98**, 141 (1994).

[3] Z. Zhang, S. Padmaja, R. D. Saini, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. **98**, 4312 (1994).

[4] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

$HO + CHF_2OCHF_2 \rightarrow H_2O + CHF_2OCF_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.47\pm0.2)\times10^{-14}$	296	Zhang *et al.*, 1992[1]	(a)
$5.4\times10^{-13}\exp[-(1560\pm202)/T]$	269–312	Garland *et al.*, 1993[2]	(b)
$(3.0\pm0.7)\times10^{-15}$	295		
Reviews and Evaluations			
3.0×10^{-15}	298	NASA, 1994[3]	(c)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO radicals.

(b) Laser photolysis system with LIF detection of HO radicals.

(c) Based on the room temperature rate coefficient of Garland *et al.*[2]

Preferred Values

$k=2.9\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

Comments on Preferred Values

The 296 K rate coefficient of Zhang *et al.*[1] is an order of magnitude higher than that of Garland *et al.*,[2] presumably due to the presence of impurities in the CHF_2OCHF_2 sample used by Zhang *et al.*[1,2] The preferred 298 K rate coefficient is derived from the absolute rate coefficients of Garland *et al.*[2]

References

[1] Z. Zhang, R. D. Saini, M. J. Kurylo, and R. E. Huie, J. Phys. Chem. **96**, 9301 (1992).

[2] N. L. Garland, L. J. Medhurst, and H. H. Nelson, J. Geophys. Res. **98**, 23107 (1993).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$HO + HC(O)F \rightarrow H_2O + FCO$

$\Delta H^\circ=-60.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$<5\times10^{-15}$	296 ± 2	Wallington and Hurley, 1993[1]	(a)

Comments

(a) Relative rate method. HO radicals generated from the photolysis of O_3-H_2-O_2 mixtures, and HC(O)F formed *in situ* from the oxidation of CH_3F. No losses of HC(O)F were observed, leading to a rate coefficient ratio of $k(HO + HC(O)F)/k(HO + CH_3F)<0.25$. This upper limit to the rate coefficient ratio is placed on an absolute basis by use of $k(HO + CH_3F)=1.95\times10^{-14}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k<1\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is derived from the sole study of Wallington and Hurley,[1] with the higher upper limit reflecting uncertainties in the reference reaction rate coefficient.

References

[1] T. J. Wallington and M. D. Hurley, Environ. Sci. Technol. **27**, 1448 (1993).

$HO + CHF_2CHO \rightarrow H_2O + CHF_2CO$ (1)
$\rightarrow H_2O + CF_2CHO$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.7\pm0.2)\times10^{-12}$	298±2	Scollard *et al.*, 1993[1]	(a)
Relative Rate Coefficients			
$(1.4\pm0.3)\times10^{-12}$	298±2	Scollard *et al.*, 1993[1]	(b)

Comments

(a) Laser photolysis system with resonance fluorescence detection of HO radicals.

(b) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO (or C_2H_5ONO)-NO-CHF_2CHO-toluene-air mixtures at 1 bar pressure. The concentrations of CHF_2CHO and toluene were measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CHF_2CHO)/k(HO + toluene)$ is placed on an absolute basis by using a rate coefficient of $k(HO + toluene)=5.96\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[2]

Preferred Values

$k=1.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

Comments on Preferred Values

The absolute and relative rate coefficients of Scollard *et al.*[1] are in good agreement, and the preferred value is the average of these rate coefficients. The reaction is expected to proceed by pathway (1).[1]

References

[1] D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, J. Phys. Chem. **97**, 4683 (1993).

[2] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 1**, 1 (1989); **Monograph 2**, 1 (1994).

$HO + CF_3CHO \rightarrow H_2O + CF_3CO$

Rate coefficient data

k/cm^3 molecule^{-1} s^1	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.5\pm0.5)\times10^{-13}$	298	Scollard *et al.*, 1993[1]	(a)
Relative Rate Coefficients			
$(5.4\pm1.2)\times10^{-13}$	298±2	Scollard *et al.*, 1993[1]	(b)
Reviews and Evaluations			
1.1×10^{-12}	298	IUPAC, 1992[2]	(c)
5.3×10^{-13}	298	Atkinson, 1994[3]	(d)

Comments

(a) Laser photolysis system with resonance fluorescence detection of HO radicals.

(b) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO (or C_2H_5ONO)-NO-CF_3CHO-CH_3COCH_3-air mixtures at 1 bar pressure. The concentrations of CF_3CHO and CH_3COCH_3 were measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CF_3CHO)/k(HO + CH_3COCH_3)$ is placed on an absolute basis by use of a rate coefficient of $k(HO + CH_3COCH_3)=2.2\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Based on the absolute rate coefficients of Dóbé *et al.*[4]

(d) Based on the (as then unpublished) relative rate coefficient of Scollard *et al.*[1]

Preferred Values

$k=6.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.20$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute and relative rate coefficients of Scollard *et al.*,[1] which are a factor of 1.7–2.0 lower than the previous absolute room temperature rate coefficient of Dóbé *et al.*[4]

References

[1] D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, J. Phys. Chem. **97**, 4683 (1993).

[2] IUPAC Supplement IV, 1992 (see references in Introduction).

[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[4] S. Dóbé, L. A. Khachatryan, and T. Bérces, Ber. Bunsenges. Phys. Chem. **93**, 847 (1989).

HO + CF_3COOH → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.6\pm0.4)\times10^{-13}$	315	Møgelberg *et al.*, 1994[1]	(a)
$(1.5\pm0.2)\times10^{-13}$	348		
Relative Rate Coefficients			
$2.0\times10^{-13}\exp[-(156\pm400)/T]$	283–323	Carr *et al.*, 1994[2]	(b,c)
$(1.18\pm0.10)\times10^{-13}$	298±2		
$(1.21\pm0.22)\times10^{-13}$	298±2	Carr *et al.*, 1994[2]	(b,d)
$(1.75\pm0.44)\times10^{-13}$	296	Møgelberg *et al.*, 1994[1]	(e)

Comments

(a) Pulsed radiolysis system with resonance absorption detection of HO radicals.

(b) Relative rate method. HO radicals were generated by the 254 nm photolysis of O_3 in the presence of water vapor in O_3-H_2O-CF_3COOH-C_2H_6 (or C_3H_8)-O_2 mixtures. The concentrations of CF_3COOH and C_2H_6 (or C_3H_8) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(HO + CF_3COOH)/k(HO + C_2H_6)=0.025\exp[(874\pm400)/T]$ (0.47 ± 0.04 at 298±2 K) and $k(HO + CF_3COOH)/k(HO + C_3H_8)=0.11\pm0.02$ at 298 K are placed on an absolute basis by using rate coefficients of $k(HO + C_2H_6)=7.9\times10^{-12}\exp(-1030/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation) and $k(HO + C_3H_8)=1.10\times10^{-12}$ cm^{-3} molecule^{-1} s^{-1} at 298 K (this evaluation).

(c) Relative to k(OH + ethane).

(d) Relative to k(OH + propane).

(e) Relative rate method. HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of H_2 in O_3-H_2-CF_3COOH-C_2H_6-O_2 mixtures at 740 Torr total pressure. The concentrations of CF_3COOH and ethane were measured by FTIR spectroscopy. The measured rate coefficient ratio was $k(HO + CF_3COOH)/k(HO + C_2H_6)=0.59\pm0.04$. If the $(CF_3COOH)_2$ dimer is unreactive towards the HO radical, then the rate coefficient ratio corrected for dimer formation is 0.84 ± 0.06.[1] An average value of $k(HO + CF_3COOH)/k(HO + C_2H_6)=0.72\pm0.18$ was preferred,[1] and is placed on an absolute basis by using a rate coefficient of $k(HO + C_2H_6)=2.43\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 296 K (this evaluation).

Preferred Values

$k=1.4\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 283–348 K.

Reliability

$\Delta\log k=\pm0.20$ over the temperature range 283–348 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the relative and absolute rate coefficients of Møgelberg *et al.*[1] and Carr *et al.*[2] The reaction is expected to proceed by overall H-atom abstraction from the -OH group to form $H_2O + CF_3CO_2$ [see the data sheets on the HO radical reactions with HC(O)OH and $CH_3C(O)OH$].

References

[1] T. E. Møgelberg, O. J. Nielsen, J. Sehested, T. J. Wallington, and M. D. Hurley, Chem. Phys. Lett. **226**, 171 (1994).

[2] S. Carr, J. J. Treacy, H. W. Sidebottom, R. K. Connell, C. E. Canosa-Mas, R. P. Wayne, and J. Franklin, Chem. Phys. Lett. **227**, 39 (1994).

$HO_2 + CH_2FO_2 \rightarrow O_2 + CH_2FO_2H$ (1)
$\rightarrow O_2 + HCOF + H_2O$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Branching Ratios			
$k_1/k=0.29\pm0.08$	295	Wallington *et al.*, 1994[1]	(a)
$k_2/k=0.71\pm0.11$	295		

Comments

(a) HO_2 and CH_2FO_2 radicals were generated from the steady-state photolysis of Cl_2 in the presence of CH_3F-H_2-air mixtures at total pressures of 300–700 Torr. The branching ratios were derived from FTIR analysis of CH_2FO_2H and HCOF, which accounted for $100\pm13\%$ of the loss of CH_3F.

Preferred Values

$k_1/k=0.3$ at 298 K.
$k_2/k=0.7$ at 298 K.

Reliability

$\Delta(k_1/k)=\Delta(k_2/k)=\pm0.1$ at 298 K.

Comments on Preferred Values

The lack of a pressure dependence of the branching ratio determined by Wallington *et al.*[1] indicates that there is no thermal decomposition of the products. The observation of two reaction channels for this reaction is in accord with data for other HO_2 reactions with substituted peroxy radicals, for example, with $HOCH_2O_2$ and $CH_3OCH_2O_2$ radicals.

References

[1] T. J. Wallington, M. D. Hurley, W. F. Schneider, J. Sehested, and O. J. Nielsen, Chem. Phys. Lett. **218**, 34 (1994).

$HO_2 + CF_3CHFO_2 \rightarrow O_2 + CF_3CHFO_2H$ (1)
$\rightarrow O_2 + CF_3COF + H_2O$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.8\times10^{-13}\exp[(910\pm220)/T]$	210-363	Maricq *et al.*, 1994[1]	(a)
$(4.7\pm1.7)\times10^{-12}$	295		
Branching Ratios			
$k_1/k > 0.95$	296	Maricq *et al.*, 1994[1]	(b)
$k_2/k < 0.05$	296		

Comments

(a) Flash photolysis time-resolved UV absorption study of F_2-CF_3CH_2F-H_2-O_2-N_2 mixtures. The rate coefficients were obtained from a fit of the decay curves for CF_3CHFO_2, HO_2, CF_3O_2, and ROOH, based on a mechanism of 14 reactions.

(b) Steady-state photolysis of Cl_2-CF_3CH_2F-H_2-O_2-N_2 mixtures with FTIR analysis of the products HCOF, CF_3COF, COF_2, and $CF_3O_3CF_3$. The branching ratio, k_2/k, cited above was based on measurements of CF_3COF, and the value of k_1/k was inferred.

Preferred Values

$k=3.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=1.8\times10^{-13}\exp(910/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210–365 K.
$k_1/k>0.95$ at 298 K.
$k_2/k<0.05$ at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

Confirmation of both the overall rate coefficient k and the branching ratios are needed. It is interesting to note that the rate coefficient is quite low for this type of reaction; any increase in the rate coefficient which might be anticipated by the presence of an α-F atom in the RO_2 radical is apparently offset by the decrease caused by the presence of the CF_3 group.

References

[1] M. M. Maricq, J. J. Szente, M. D. Hurley, and T. J. Wallington, J. Phys. Chem. **98**, 8962 (1994).

$FO + O_3 \rightarrow F + 2O_2$ (1)

$\rightarrow FO_2 + O_2$ (2)

$\Delta H^\circ(1) = -172\ kJ\cdot mol^{-1}$
$\Delta H^\circ(2) = -226\ kJ\cdot mol^{-1}$

No new data have been published since our last evaluation.

Comments

The $FO + O_3$ reaction has two possible pathways which are exothermic, resulting in the production of $F + 2O_2$ or $FO_2 + O_2$. Although this reaction has not been studied in a simple direct manner, two studies of complex chemical systems have provided some relevant kinetic information. Starrico *et al.*[1] measured quantum yields for ozone destruction in F_2/O_3 mixtures, and attributed the high values, ~4600, to be due to the rapid regeneration of atomic fluorine via the $FO + O_3 \rightarrow F + 2O_2$ reaction. However, their results are probably also consistent with the chain propagation process being $FO + FO \rightarrow 2F + O_2$ (the latter reaction has been studied twice (by Wagner *et al.*[2] and Clyne and Watson[3]) but although the value of $[F]_{produced}/[FO]_{consumed}$ is known to be close to unity it has not been accurately determined). Consequently it is impossible to ascertain from the experimental results of Starrico *et al.*[1] whether or not the high quantum yields for ozone destruction should be attributed to the $FO + O_3$ reaction producing either $F + 2O_2$ or $FO_2 + O_2$ (this process is also a chain propagation step if the resulting FO_2 radical preferentially reacts with ozone rather than with either FO or itself). Wagner *et al.*[2] utilized a low pressure discharge flow-mass spectrometric system to study the $F + O_3$ and $FO + FO$ reactions by directly monitoring the time history of the concentrations of F, FO, and O_3. They concluded that the $FO + O_3$ reaction was unimportant in their system. However, their paper does not present enough information to warrant this conclusion. Indeed, their value of $k(FO + FO)$ of 3×10^{-11} cm^3 $molecule^{-1}$ s^{-1} is about a factor of 4 greater than that reported by Clyne and Watson,[3] which may possibly be attributed to either reactive impurities being present in their system, e.g., $O(^3P)$, or that the $FO + O_3$ reactions were not of negligible importance in their study. Consequently, it is not possible to determine a value for the $FO + O_3$ reaction rate constant from existing experimental data. It is worth noting that the analogous $ClO + O_3$ reaction is reported[4] to be extremely slow ($<10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}), and upper limits of 8×10^{-14} cm^3 $molecule^{-1}$ s^{-1} (Ref. 5) and 5×10^{-15} cm^3 $molecule^{-1}$ s^{-1} [6] have been reported for $k(BrO + O_3)$.

Preferred Values

None.

References

[1] E. H. Starrico, S. E. Sicre, and H. J. Schumacher, Z. Physik Chem. N.F. **31**, 385 (1962).
[2] H. Gg. Wagner, C. Zetzsch, and J. Warnatz, Ber. Bunsenges. Phys. Chem. **76**, 526 (1972).
[3] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **70**, 1109 (1974).
[4] W. B. DeMore, C. L. Lin, and S. Jaffe, results presented at ACS meeting Philadelphia, 1975, and 12th Informal Conference on Photochemistry, Washington, D.C. (1976).
[5] M. A. A. Clyne and H. W. Cruse, Trans. Faraday Soc. **66**, 2214 (1970).
[6] S. P. Sander and R. T. Watson, J. Phys. Chem. **85**, 4000 (1981).

$FO + NO \rightarrow F + NO_2$

$\Delta H° = -87$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.6\pm0.5)\times10^{-11}$	298	Ray and Watson, 1981[1]	(a)
$1.86\times10^{-11}(T/300)^{-(0.66\pm0.13)}$	300–845	Bedzhanyan, Markin, and Gershenzon, 1993[2]	(b)
$(1.9\pm0.4)\times10^{-11}$	300		
Reviews and Evaluations			
2.6×10^{-11}	298	IUPAC, 1992[3]	(c)
$8.2\times10^{-12}\exp(300/T)$	200–300	NASA, 1994[4]	(d)

Comments

(a) Discharge flow system with MS detection of FO.
(b) Discharge flow system. Pseudo-first-order decays of FO radicals in excess NO were monitored by LMR.
(c) Based on the data of Ray and Watson.[1]
(d) Based on the data of Ray and Watson[1] and Bedzhanyan *et al.*[2]

Preferred Values

$k=2.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=8.2\times10^{-12}\exp(300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–850 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.

$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The preferred room temperature value is the average of the room temperature values from the only two studies.[1,2] The temperature dependence is derived from a fit to the data of Bedzhanyan *et al.*[2] and the *A*-factor is fitted to the preferred room temperature valve. The temperature dependence is similar to that for the analogous ClO and BrO radical reactions.

References

[1] G. W. Ray and R. T. Watson, J. Phys. Chem. **85**, 2955 (1981).
[2] Yu. R. Bedzhanyan, E. M. Markin, and Yu. M. Gershenzon, Kinetics and Catalysis **34**, 1 (1993); original pages 7–10 (1993).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

$FO + FO \rightarrow 2F + O_2$ (1)
$\rightarrow FO_2 + F$ (2)
$\rightarrow F_2 + O_2$ (3)

$\Delta H°(1) = -59$ kJ·mol^{-1}
$\Delta H°(2) = -113$ kJ·mol^{-1}
$\Delta H°(3) = -218$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2+k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.0\times10^{-11}(T/300)^{0.85\pm0.5}$	300–435	Bedzhanyan, Markin, and Gershenzon, 1993[1]	(a)
Reviews and Evaluations			
1.5×10^{-11}	298	IUPAC, 1992[2]	(b)
1.0×10^{-11}	298–435	NASA, 1994[3]	(c)

Comments

(a) Discharge flow system with a combined EPR/IR LMR spectrometer.
(b) Based on the data of Clyne and Watson[4] and Wagner *et al.*[5]

(c) Based on the data of Bezhanyan *et al.*[1] and Clyne and Watson.[4]

Preferred Values

$k = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 298–435 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

The recommended value is based on the results of Bedzhanyan *et al.*[1] and Clyne and Watson.[4] In a less direct study, Wagner *et al.*[5] reported a higher value. Although Bedzhanyan *et al.*[1] report a weak temperature dependence, a temperature-independent value fits their data equally well and is recommended in this evaluation. This study[1] shows that the predominant reaction channel is that to produce 2F + O_2.

References

[1] Yu. R. Bedzhanyan, E. M. Markin, and Yu. M. Gershenzon, Kinetics and Catalysis **33**, 601 (1993).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **70**, 1109 (1974).
[5] H. Gg. Wagner, C. Zetzsch, and J. Warnatz, Ber. Bunsenges. Phys. Chem. **76**, 526 (1972).

$FO_2 + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<3.4 \times 10^{-16}$	298	Sehested *et al.*, 1994[1]	(a)
Reviews and Evaluations			
$<3.4 \times 10^{-16}$	298	NASA, 1994[2]	(b)

Comments

(a) Pulse radiolysis/UV absorption spectroscopy technique. Pulse radiolysis of O_3-O_2-SF_6 mixtures in a high pressure cell at 18 bar of SF_6. The decay of FO_2 radicals was monitored in absorption at 220 nm.
(b) Based on the results of Sehested *et al.*[1]

Preferred Values

$k < 3.4 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred room temperature upper limit is based on results of the pulse radiolysis/UV absorption study of Sehested *et al.*[1] This is the sole reported study of this reaction rate coefficient.

References

[1] J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, J. Phys. Chem. **98**, 6731 (1994).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$FO_2 + NO \rightarrow FNO + O_2$

$\Delta H^\circ = -182$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.1) \times 10^{-12}$	298	Sehested *et al.*, 1994[1]	(a)
Reviews and Evaluations			
1.5×10^{-12}	298	NASA, 1994[2]	(b)

Comments

(a) Pulse radiolysis/UV absorption spectroscopy technique. Pulse radiolysis of NO-O_2-SF_6 mixtures in a low pressure cell at 1 bar SF_6. The formation of FNO was monitored in absorption at 310.5 nm. The yield of FNO was determined to be 100±14%.

(b) Based on the results of Sehested *et al.*[1]

Preferred Values

$k=1.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.5$ at 298 K.

Comments on Preferred Values

The preferred room temperature rate coefficient is based on results of the pulse radiolysis/UV absorption study of Sehested *et al.*[1] This is the sole reported study of this reaction rate coefficient.

References

[1] J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, J. Phys. Chem. **98**, 6731 (1994).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$FO_2 + NO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.05\pm0.15)\times10^{-13}$	298	Sehested *et al.*, 1994[1]	(a)
Reviews and Evaluations			
1.0×10^{-13}	298	NASA, 1994[2]	(b)

Comments

(a) Pulse radiolysis/UV absorption spectroscopy technique. Pulse radiolysis of NO_2-O_2-SF_6 mixtures in a low pressure cell at 1 bar SF_6 and also in a high pressure cell at 18 bar SF_6. The decay of NO_2 was monitored in absorption at 400 nm, and that of FO_2 at 220 nm. The rate coefficient showed no dependence on pressure over the pressure range 1 to 18 bar SF_6.

(b) Based on the results of Sehested *et al.*[1]

Preferred Values

$k=1.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.5$ at 298 K.

Comments on Preferred Values

The preferred room temperature rate coefficient is based on results of the pulse radiolysis/UV absorption study of Sehested *et al.*[1] This is the sole reported study of this reaction rate coefficient. Although the products have not been determined, this reaction can be expected to yield either FO_2NO_2 or $FNO_2 + O_2$.

References

[1] J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, J. Phys. Chem. **98**, 6731 (1994).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$FO_2 + CO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<5.1\times10^{-16}$	298	Sehested *et al.*, 1994[1]	(a)
Reviews and Evaluations			
$<5.1\times10^{-16}$	298	NASA, 1994[2]	(b)

Comments

(a) Pulse radiolysis/UV absorption spectroscopy technique. Pulse radiolysis of CO-O_2-SF_6 mixtures in a high pressure cell at 18 bar SF_6. The decay of FO_2 radicals was monitored in absorption at 220 nm.
(b) Based on the results of Sehested *et al.*[1]

Preferred Values

$k<5.1\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred room temperature upper limit is based on results of the pulse radiolysis/UV absorption study of Sehested *et al.*[1] This is the sole reported study of this reaction rate coefficient.

References

[1] J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, J. Phys. Chem. **98**, 6731 (1994).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$FO_2 + CH_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<4.1\times10^{-15}$	298	Sehested *et al.*, 1994[1]	(a)
Reviews and Evaluations			
$<4.1\times10^{-15}$	298	NASA, 1994[2]	(b)

Comments

(a) Pulse radiolysis/UV absorption spectroscopy technique. Pulse radiolysis of CH_4-O_2-SF_6 mixtures in a high pressure cell at 18 bar SF_6. The decay of FO_2 radicals was monitored in absorption at 220 nm.
(b) Based on the results of Sehested *et al.*[1]

Preferred Values

$k<4.1\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred room temperature upper limit is based on results of the pulse radiolysis/UV absorption study of Sehested *et al.*[1] This is the sole reported study of this reaction rate coefficient.

References

[1] J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, J. Phys. Chem. **98**, 6731 (1994).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CF_3 + O_2 + M \rightarrow CF_3O_2 + M$

$\Delta H^\circ = -146.6$ kJ·mol^{-1}

Low-pressure rate coefficient

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.9\times10^{-29}\ (T/300)^{-4.7}\ [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_0 = \pm0.2$ at 298 K.

$\Delta n = \pm1$.

Comments on Preferred Values

There is good agreement between Refs. 1 and 2 for M =He. The falloff extrapolation uses $F_c = 0.6$.

High-pressure rate coefficient

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–400 K.

Comments on Preferred Values

The preferred values are from Ref. 3 because these measurements were done relatively close to the high pressure limit. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] F. Caralp, R. Lesclaux, and A. M. Dognon, Chem. Phys. Lett. **129**, 433 (1986).

[2] K. R. Ryan and I. C. Plumb, J. Phys. Chem. **86**, 4678 (1982).

[3] R. Cooper, J. B. Cumming, S. Gordon, and W. A. Mulac, Rad. Phys. Chem. **16**, 169 (1980).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CF_3O + O_2 \rightarrow COF_2 + FO_2$

$\Delta H^\circ = 47.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<2 \times 10^{-17}$	298	Turnipseed, Barone, and Ravishankara, 1994[1]	(a)
$<4 \times 10^{-17}$	373		
Reviews and Evaluations			
$<3 \times 10^{-11} \exp(-5000/T)$	250–370	NASA, 1994[2]	(b)

Comments

(a) Pulsed laser photolysis/pulsed laser-induced fluorescence technique. CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.

(b) Based on the results of Turnipseed *et al.*[1]

Preferred Values

$k < 1 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k < 1 \times 10^{-10} \exp(-5600/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.

Comments on Preferred Values

The preferred values are based on the upper limit at 373 K reported by Turnipseed *et al.*[1] Assuming that the activation energy barrier is at least equal to the reaction endothermicity (5600 K) leads to the preferred limits given for the *A*-factor and for k(298 K). This procedure using the high temperature limit yields a room temperature limit an order of magnitude lower than the upper limit to the rate coefficient directly determined at 298 K. Chen *et al.*[3] in a long path FTIR study of the reaction of CF_3O with NO found no evidence for the reaction of CF_3O with O_2 in 1 bar of air at room temperature.

References

[1] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **98**, 4594 (1994).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

[3] J. Chen, T. Zhu, and H. Niki, J. Phys. Chem. **96**, 6115 (1992).

$CF_3O + O_3 \rightarrow CF_3O_2 + O_2$

$\Delta H° = -101.1\ kJ \cdot mol^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<1\times10^{-13}$	295	Nielsen and Sehested, 1993[1]	(a)
$<5\times10^{-14}$	210–353	Maricq and Szente, 1993[2]	(b)
$<2\times10^{-15}$	298	Fockenberg, Saathoff, and Zellner, 1994[3]	(c)
$<4\times10^{-14}$	298	Ravishankara *et al.*, 1994[4]	(d)
$(2.5^{+0.7}_{-1.5})\times10^{-14}$	298	Turnipseed, Barone, and Ravishankara, 1994[5]	(e)
$(3.7\pm1.5)\times10^{-14}$	373		
Relative Rate Coefficients			
$<3\times10^{-14}$	295	Wallington, Hurley, and Schneider, 1993[6]	(f)
Reviews and Evaluations			
$2\times10^{-12}\exp(-1300/T)$	250–370	NASA, 1994[7]	(g)

Comments

(a) Pulse radiolysis/UV absorption technique. Radicals generated by pulse radiolysis of CHF_3-O_2-O_3-SF_6 mixtures. Upper limit for k derived from simulations of ozone absorption transients at 254 nm and 276 nm in the presence of CF_3O and CF_3O_2 radicals.

(b) Flash photolysis/UV absorption technique. Radicals generated by 351 nm photolysis of F_2 in a flowing F_2-CHF_3-O_3-O_2-N_2 mixture. O_3 and CF_3O_2 radicals were monitored by absorption at 255 nm, and 210 nm, respectively.

(c) Laser photolysis/laser-induced fluorescence technique. CF_3O radicals were generated by excimer laser photolysis of CF_3OCl at 351 nm.

(d) Flow tube reactor/chemical ionization mass spectrometer technique. CF_3O radicals were generated by pyrolysis of CF_3OOCF_3.

(e) Pulsed laser photolysis/pulsed laser-induced fluorescence technique. CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.

(f) Relative rate technique. Radicals generated by visible photolysis of CF_3NO/O_3 mixtures in 700 Torr O_2. Analysis was by FTIR spectroscopy. Value of k was derived by authors from the measured ratio $k/k(CF_3O + NO_2)$ and an estimated value of $k(CF_3O + NO_2)$.

(g) Based on the results of Turnipseed *et al.*[5]

Preferred Values

$k = 2.5\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2\times10^{-12}\exp(-1300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.

Reliability

$\Delta \log k = \pm 1$ at 298 K.

$\Delta(E/R) = \pm 600$ K.

Comments on Preferred Values

This evaluation accepts the recommendation of the NASA Panel for Data Evaluation.[7] The preferred value of k at 298 K is based on the results of Turnipseed *et al.*[5] Using a similar technique, Fockenberg *et al.*[3] reported a room temperature value an order of magnitude lower. The higher value of Turnipseed *et al.*[5] is recommended for use in atmospheric models, but it should be stressed that the true value may be substantially lower. Upper limits reported in the studies of Nielsen and Sehested,[1] Maricq and Szente,[2] Ravishankara *et al.*,[4] and Wallington *et al.*[5] are all consistent with the recommendation. Because of the large uncertainties in the two values of Turnipseed *et al.*,[5] Arrhenius parameters have not been derived using these values. Rather, the recommended A factor has been estimated by analogy with other CF_3O reactions, and the value of E/R fitted to the preferred room temperature value.

References

[1] O. J. Nielsen and J. Sehested, Chem. Phys. Lett. **213**, 433 (1993).

[2] M. M. Maricq and J. J. Szente, Chem. Phys. Lett. **213**, 449 (1993).

[3] C. Fockenberg, H. Saathoff, and R. Zellner, Chem. Phys. Lett. **218**, 21 (1994).

[4] A. R. Ravishankara, A. A. Turnipseed, N. R. Jensen, S. Barone, M. Mills, C. J. Howard, and S. Solomon, Science **263**, 71 (1994).

[5] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **98**, 4594 (1994).

[6] T. J. Wallington, M. D. Hurley, and W. F. Schneider, Chem. Phys. Lett. **213**, 442 (1993).

[7] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CF_3O + H_2O \rightarrow CF_3OH + HO$

$\Delta H° = 43.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<1\times10^{-16}$	298	Turnipseed *et al.*, 1995[1]	(a)
$<2\times10^{-16}$	381		
Relative Rate Coefficients			
$>2\times10^{-18}$	296	Wallington *et al.*, 1993[2]	(b)
$<4\times10^{-16}$	296		
Reviews and Evaluations			
$<3\times10^{-12}$ exp($-3600/T$)	250–380	NASA, 1994[3]	(c)

Comments

(a) Pulsed laser photolysis/pulsed laser induced fluorescence technique. CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.

(b) Long path FTIR-based study. CF_3O radicals generated by chlorine-initiated oxidation of CF_3CFH_2 (HFC-134a) in photolytic mixture of Cl_2-CF_3CFH_2-H_2O in 700 Torr air. Reaction rate studied in competition with the rate of $CF_3O + CF_3CFH_2$.

(c) Based on the results of Turnipseed *et al.*[1] at 381 K and an estimated *A*-factor.

Preferred Values

$k < 2\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k < 3\times10^{-12}$ exp($-3600/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 250–380 K.

Comments on Preferred Values

This evaluation accepts the recommendation of the NASA Panel for Data Evaluation.[3] The *A*-factor is estimated by analogy with similar reactions of CF_3O and the activation energy is fitted to the upper limit at 381 K reported by Turnipseed *et al.*[1] Note that this procedure results in a lower limit for E/R ($E/R > 3600$ K). The preferred value of k (298 K) is calculated from the Arrhenius parameters. The limits reported by Wallington *et al.*[2] are consistent with this preferred value.

References

[1] A. A. Turnipseed, S. B. Barone, N. R. Jensen, D. R. Hanson, C. J. Howard, and A. R. Ravishankara, J. Phys. Chem. **99**, 6000 (1995).

[2] T. J. Wallington, M. D. Hurley, W. F. Schneider, J. Sehested, and O. J. Nielsen, J. Phys. Chem. **97**, 7606 (1993).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CF_3O + NO \rightarrow COF_2 + FNO$

$\Delta H° = -135$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.2\pm2.7)\times10^{-11}$	295	Sehested and Nielsen, 1993[1]	(a)
3.34×10^{-11} exp[$(160\pm45)/T$]	233–360	Turnipseed, Barone, and Ravishankara, 1994[2]	(b)
$(5.62\pm0.74)\times10^{-11}$	298		
4.1×10^{-11} exp[$(60\pm100)/T$]	231–393	Jensen, Hanson, and Howard, 1994[3]	(c)
$(5.0\pm1.0)\times10^{-11}$	298		
Reviews and Evaluations			
3.7×10^{-11} exp($110/T$)	230–390	NASA, 1994[4]	(d)

Comments

(a) Pulse radiolysis/UV absorption technique. Radicals generated by pulse radiolysis of CHF_3-O_2-NO-SF_6 mixtures. Value of k derived from simulations of FNO absorption transients at 310.5 nm.

(b) Pulsed laser photolysis/pulsed laser-induced fluorescence technique. CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.

(c) Flow tube reactor/chemical ionization mass spectrometer technique. CF_3O radicals were generated by pyrolysis of CF_3OOCF_3. A low value of k from the same laboratory reported earlier by Bevilacqua *et al.*[5] is superseded by these results.

(d) Based on the results of Turnipseed *et al.*,[2] Jensen *et al.*,[3] and Sehested and Nielsen.[1]

Preferred Values

$k=5.4\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k=3.7\times10^{-11}$ $\exp(110/T)$ cm^3 molecule ^{1} s ^{1} over the temperature range 230–390 K.

Reliability

$\Delta\log k=\pm0.1$ at 298 K.
$\Delta(E/R)=\pm100$ K.

Comments on Preferred Values

This evaluation accepts the recommendation of the NASA Panel for Data Evaluation.[4] The preferred values are based on the 233–360 K values of Turnipseed *et al.*,[2] the 231–393 K values of Jensen *et al.*,[3] and the 295 K value of Sehested and Nielsen.[1] These results are in good agreement. The low value of k reported by Bevilacqua *et al.*[5] has been superseded by the results of Jensen *et al.*[3] The reaction products have been reported by Chen *et al.*,[6] Bevilacqua *et al.*,[5] and Li and Francisco.[7]

References

[1] J. Sehested and O. J. Nielsen, Chem. Phys. Lett. **206**, 369 (1993).
[2] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **98**, 4594 (1994).
[3] N. R. Jensen, D. R. Hanson, and C. J. Howard, J. Phys. Chem. **98**, 8574 (1994).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] T. J. Bevilacqua, D. R. Hanson, and C. J. Howard, J. Phys. Chem. **97**, 3750 (1993).
[6] J. Chen, T. Zhu, and H. Niki, J. Phys. Chem. **96**, 6115 (1992).
[7] Z. Li and J. S. Francisco, Chem. Phys. Lett. **186**, 336 (1991).

$CF_3O + CH_4 \rightarrow CF_3OH + CH_3$

$\Delta H^\circ=-16.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.2\pm0.2)\times10^{-14}$	298	Saathoff and Zellner, 1993[1]	(a)
$1.92\times10^{-12}\exp[-(1370\pm85)/T]$	247–360	Barone, Turnipseed, and Ravishankara, 1994[2]	(b)
$(1.93\pm0.11)\times10^{-14}$	298		
$3.1\times10^{-12}\exp[-(1470\pm250)/T]$	231–385	Jensen, Hanson, and Howard, 1944[3]	(c)
$(2.2\pm0.4)\times10^{-14}$	298		
Relative Rate Coefficients			
$<5\times10^{-15}$	297	Chen *et al.*, 1992[4]	(d)
$(1.2\pm0.1)\times10^{-14}$	298	Kelly *et al.*, 1993[5]	(e)
Reviews and Evaluations			
$2.5\times10^{-12}\exp(-1420/T)$	230–380	NASA, 1994[6]	(f)

Comments

(a) Laser photolysis/laser induced fluorescence technique. CF_3O radicals were generated by photolysis of CF_3OF at 248 nm.

(b) Pulsed laser photolysis/pulsed laser induced fluorescence technique. CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.

(c) Flow tube reactor/chemical ionization mass spectrometer technique. CF_3O radicals were generated by pyrolysis of CF_3OOCF_3.

(d) Long path FTIR-based product study of visible photolysis of CF_3NO-NO-CH_4 mixtures in 700 Torr air. Searched for CH_2O product from oxidation of CH_4 initiated by reaction of CF_3O radicals with CH_4. Upper limit of k given in table is derived from the measured ratio $k/k(CF_3O + NO)<10^{-4}$ and the value of $k(CF_3O + NO)$ given in this evaluation.

(e) Long-path FTIR-based study. CF_3O radicals were generated by photolysis of CF_3OOCF_3. The decay of the reactant hydrocarbon was compared with the decay of the reference hydrocarbon. The value of k given in the table is derived from the measured ratio

$k/k(CF_3O + C_2H_6) = 0.010 \pm 0.001$ and the value of $k(CF_3O + C_2H_6)$ given in this evaluation.

(f) Based on the results of Saathoff and Zellner,[1] Barone *et al.*,[2] and Jensen *et al.*[3]

Preferred Values

$k = 2.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.5 \times 10^{-12} \exp(-1420/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–380 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This evaluation accepts the recommendation of the NASA Panel for Data Evaluation.[6] The preferred value at room temperature is the average of the values reported by Saathoff and Zellner,[1] Barone *et al.*,[2] and Jensen *et al.*[3] The temperature dependence is based on the 247–360 K data of Barone *et al.*[2] and the 231–385 K data of Jensen *et al.*[3] Results of these three direct studies are in excellent agreement. The relative rate measurements of Chen *et al.*[4] and Kelly *et al.*[5] are factors of 4 and 2, respectively, lower than the preferred value. Jensen *et al.*[3] detected the product CF_3OH by chemical ionization mass spectrometer (CIMS) and observed its formation to correlate with the loss of the CF_3O reactant. The CF_3OH product of this reaction was also observed by Bevilacqua *et al.*[7]

References

[1] H. Saathoff and R. Zellner, Chem. Phys. Lett. **206**, 349 (1993).

[2] S. B. Barone, A. A. Turnipseed, and A. R. Ravishankara, J. Phys. Chem. **98**, 4602 (1994).

[3] N. R. Jensen, D. R. Hanson, and C. J. Howard, J. Phys. Chem. **98**, 8574 (1994).

[4] J. Chen, T. Zhu, H. Niki, and G. J. Mains, Geophys. Res. Lett. **19**, 2215 (1992).

[5] C. Kelly, J. Treacy, H. W. Sidebottom, and O. J. Nielsen, Chem. Phys. Lett. **207**, 498 (1993).

[6] NASA Evaluation No. 11, 1994 (see references in Introduction).

[7] T. J. Bevilacqua, D. R. Hanson, and C. J. Howard, J. Phys. Chem. **97**, 3750 (1993).

$CF_3O + C_2H_6 \rightarrow CF_3OH + C_2H_5$

$\Delta H° = -32.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.2) \times 10^{-12}$	298	Saathoff and Zellner, 1993[1]	(a)
$4.84 \times 10^{-12} \exp[-(400 \pm 70)/T]$	233–360	Barone, Turnipseed, and Ravishankara, 1994[2]	(b)
$(1.30 \pm 0.11) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(1.1 \pm 0.6) \times 10^{-12}$	297	Chen *et al.*, 1992[3]	(c)
Reviews and Evaluations			
$4.7 \times 10^{-12} \exp(-400/T)$	230–360	NASA, 1994[4]	(d)

Comments

(a) Laser photolysis/laser induced fluorescence technique. CF_3O radicals were generated by the photolysis of CF_3OF at 248 nm.

(b) Pulsed laser photolysis/pulsed laser induced fluorescence technique. CF_3O radicals were generated by the photolysis of CF_3OOCF_3 at 193 nm.

(c) Long path FTIR-based product study of visible photolysis of CF_3NO-NO-C_2H_6 mixtures in 700 Torr air. The upper limit of k given in table is derived from measured ratio $k/k(CF_3O + NO) = 0.02 \pm 0.006$ and the value of $k(CF_3O + NO)$ given in this evaluation.

(d) Based on the results of Saathoff and Zellner[1] and Barone *et al.*[2]

Preferred Values

$k = 1.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.7 \times 10^{-12} \exp(-400/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–360 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This evaluation accepts the recommendation of the NASA Panel for Data Evaluation.[4] The preferred value at room temperature is the average of the values reported by Saathoff and Zellner[1] and Barone *et al.*[2] The temperature dependence is based on the 233–360 K data of Barone *et al.*[2] Results of these direct studies are in excellent agreement. The relative rate measurement of Chen *et al.*[3] is in good agreement with the preferred value. Kelly *et al.*[5] used a relative rate method with FTIR detection to determine the rate of CF_3O reaction with a number of hydrocarbons relative to the rate of the reaction of CF_3O with C_2H_6. They reported $k(CF_3O + CH_4)/k = 0.010 \pm 0.001$ at 298 K and 1 bar pressure.[5] This is nearly a factor of 2 lower than the ratio of the preferred values given in this evaluation (0.018).

References

[1] H. Saathoff and R. Zellner, Chem. Phys. Lett. **206**, 349 (1993).
[2] S. B. Barone, A. A. Turnipseed, and A. R. Ravishankara, J. Phys. Chem. **98**, 4602 (1994).
[3] J. Chen, T. Zhu, H. Niki, and G. J. Mains, Geophys. Res. Lett. **19**, 2215 (1992).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] C. Kelly, J. Treacy, H. W. Sidebottom, and O. J. Nielsen, Chem. Phys. Lett. **207**, 498 (1993).

$R_1(R_2)CHO + O_2 \rightarrow R_1COR_2 + HO_2$ or $\rightarrow$ products (1)
$R_1(R_2)CHO + M \rightarrow R_1CHO + R_2 + M$ (2)

(R = alkyl, halogenated alkyl, H or halogen atom)

Rate coefficient data

Reactions	$k_1 \cdot k_2^{-1}$/ cm^3 molecule^{-1}	Temp./K	Reference	Comments
$CH_2FO + O_2 \rightarrow HCOF + HO_2$ (1)	k_1 $[O_2] \gg k_2$ (700 Torr, air)	298	Edney and Driscoll, 1992[1]	(a)
$CH_2FO + M \rightarrow HCOF + H + M$ (2)	k_1 $[O_2] \gg k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993[2]	(a)
$CH_3CF_2O + O_2 \rightarrow$ products (1)	k_1 $[O_2] \ll k_2$ (700 Torr, air)	298	Edney and Driscoll, 1992[1]	(b)
$CH_3CF_2O + M \rightarrow CH_3 + COF_2 + M$ (2)	k_1 $[O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993[2]	(c)
$CH_2FCHFO + O_2 \rightarrow CH_2FCOF + HO_2$ (1)	k_1 $[O_2] \gg k_2$ (700 Torr, air)	296	Wallington *et al.*, 1994[3]	(d)
$CH_2FCHFO + M \rightarrow CH_2F + HCOF + M$ (2)				
$CF_3CHFO + O_2 \rightarrow CF_3COF + HO_2$ (1)	$1.58\times10^{-25}\exp(3600/T)$	261–353	Wallington *et al.*, 1992[4]	(e)
$CF_3CHFO + M \rightarrow CF_3 + HCOF + M$ (2)	2.8×10^{-20} (2 atm)	298		
	$3.2\times10^{-25}\exp(3510/T)$	273–320	Tuazon and Atkinson, 1993[5]	(f)
	4.5×10^{-20} (740 Torr)	298		
	$k_1 = 3.7\times10^{7}\exp(-2200/T)\mathrm{s}^{-1}$	211–372	Maricq and Szente, 1992[6]	(g)
	$k_1=2.3\times10^{4}\ \mathrm{s}^{-1}$ (230 Torr)	298		
	$1.18\times10^{-24}\exp(2860/T)$	235–318	Rattigan *et al.*, 1994[7]	(h)
	1.7×10^{-20} (1 atm)	298		
$CF_3CF_2O + O_2 \rightarrow$ products (1)	k_1 $[O_2] \ll k_2$ (700 Torr, air)	298	Edney and Driscoll, 1992[1]	(i)
$CF_3CF_2O + M \rightarrow CF_3 + COF_2 + M$ (2)	k_1 $[O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993[2]	(j)
$CHFClO + O_2 \rightarrow COFCl + HO_2$ (1)	k_1 $[O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993[2]	(k)
$CHFClO + M \rightarrow HCOF + Cl + M$ (2)				
$CF_2ClO + O_2 \rightarrow$ products (1)	k_1 $[O_2] \ll k_2$ (700 Torr, air)	298	Edney and Driscoll, 1992[1]	(l)
$CF_2ClO + M \rightarrow COF_2 + Cl + M$ (2)	k_1 $[O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993[2]	(m)
$CFCl_2O + O_2 \rightarrow$ products (1)	k_1 $[O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993[2]	(n)
$CFCl_2O + M \rightarrow COFCl + Cl + M$ (2)				
$CF_2ClCH_2O + O_2 \rightarrow CF_2ClCHO + HO_2$ (1)	k_1 $[O_2] \gg k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1994[8]	(o)
$CF_2ClCH_2O + M \rightarrow CF_2Cl + HCHO + M$ (2)				
$CFCl_2CH_2O + O_2 \rightarrow CFCl_2CHO + HO_2$ (1)	k_1 $[O_2] \gg k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1994[8]	(p)
$CFCl_2CH_2O + M \rightarrow CFCl_2 + HCHO + M$ (2)				
$CF_3CFClO + O_2 \rightarrow$ products (1)	k_1 $[O_2] \ll k_2$ (700 Torr, air)	298	Edney and Driscoll, 1992[1]	(q)
$CF_3CFClO + M \rightarrow CF_3COF + Cl + M$ (2)	k_1 $[O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993[2]	(r)
$CF_3CCl_2O + O_2 \rightarrow$ products (1)	k_1 $[O_2] \ll k_2$ (700 Torr, air)	296	Edney, Gay, and Driscoll, 1991[9]	(s)
$CF_3CCl_2O + M \rightarrow CF_3COCl + Cl + M$ (2)	k_1 $[O_2] \ll k_2$ (102 Torr, O_2)	298	Sato and Nakamura, 1991[10]	(t)
	k_1 $[O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993[2]	(u)
	k_1 $[O_2] \ll k_2$ (~1 atm, air)	298	Hayman *et al.*, 1993[11]	(v)
$CF_3CF_2CCl_2O + O_2 \rightarrow$ products (1)	k_1 $[O_2] \ll k_2$ (102 Torr, O_2)	298	Sato and Nakamura, 1991[10]	(w)
$CF_3CF_2CCl_2O + M \rightarrow CF_3CF_2COCl + Cl + M$ (2)	k_1 $[O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1994[8]	(x)
$CF_2ClCF_2CFClO + O_2 \rightarrow$ products (1)	k_1 $[O_2] \ll k_2$ (102 Torr, O_2)	298	Sato and Nakamura, 1991[10]	(y)
$CF_2ClCF_2CFClO + M \rightarrow CF_2ClCF_2COF + Cl + M$ (2)	k_1 $[O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1994[8]	(z)

Rate coefficient data—Continued

Reactions	$k_1 \cdot k_2^{-1}$/ cm^3 molecule^{-1}	Temp./K	Reference	Comments
$CH_2ClO + O_2 \rightarrow HCOCl + HO_2$ (1)	4.6×10^{-18} (700 Torr, $O_2 + N_2$)	296	Kaiser and Wallington, 1993[12]	(aa)
$CH_2ClO + M \rightarrow HCO + HCl + M$ (2)				
$CH_3CHClO + O_2 \rightarrow CH_3COCl + HO_2$ (1)	$k_1 [O_2] \ll k_2$ (700 Torr, air)	295	Shi, Wallington, and Kaiser, 1993[13]	(bb)
$CH_3CHClO + M \rightarrow CH_3CO + HCl + M$ (2)	$k_1 [O_2] \ll k_2$ (760 Torr, air)	298	Maricq *et al.*, 1993[14]	(cc)
$HOCH_2CHClO + O_2 \rightarrow HOCH_2COCl + HO_2$ (1)	$k_1 [O_2] \ll k_2$ (740 Torr, air)	298	Tuazon *et al.*, 1988[15]	(dd)
$HOCH_2CHClO + M \rightarrow CH_2OH + HCOCl + M$ (2)				
$HOCHClCH_2O + O_2 \rightarrow HOCHClCHO + HO_2$ (1)	$k_1 [O_2] \ll k_2$ (740 Torr, air)	298	Tuazon *et al.*, 1988[15]	(dd)
$HOCHClCH_2O + M \rightarrow CHClOH + HCHO + M$ (2)				
$CH_3CCl_2O + O_2 \rightarrow$ products (1)	$k_1 [O_2] \ll k_2$ (700 Torr, O_2)	298	Nelson *et al.*, 1990[16]	(ee)
$CH_3CCl_2O + M \rightarrow CH_3COCl + Cl + M$ (2)				
$CCl_3CH_2O + O_2 \rightarrow CCl_3CHO + HO_2$ (1)	$k_1 [O_2] \gg k_2$ (100 Torr, O_2)	298	Nelson *et al.*, 1990[16]	(ff)
$CCl_3CH_2O + M \rightarrow CCl_3 + HCHO + M$ (2)				
$CCl_3CCl_2O + O_2 \rightarrow$ products (1)	$k_1 [O_2] \ll k_2$	298	Sato and Nakamura, 1991[10]	(gg)
$CCl_3CCl_2O + M \rightarrow CCl_3COCl + Cl + M$ (2)				

Comments

(a) Steady-state photolyses of Cl_2 in the presence of CH_3F-air mixtures (1 atm) with FTIR absorption spectroscopic analyses; a 100% yield of HCOF was observed, consistent with $k_1[O_2] \gg k_2$.

(b) Steady-state photolysis of Cl_2 in the presence of CH_3CHF_2-air mixtures (1 atm) with FTIR absorption spectroscopic analyses; a 100±5% yield of COF_2 was observed, consistent with $k_1[O_2] \ll k_2$.

(c) Similar experiments to those of Comment (b); a 92.2 ±1.2% yield of COF_2 plus other unidentified products was observed, consistent with $k_1[O_2] \ll k_2$.

(d) Steady-state photolysis of Cl_2 in the presence of CH_2FCH_2F-air mixtures (700 Torr) with FTIR analysis; a 91±10% yield of HCOF was observed, consistent with $k_1[O_2] \ll k_2$.

(e) Steady-state photolyses of Cl_2 in the presence of CF_3CFH_2-O_2-N_2 mixtures at total pressures of 2 atm with FTIR analyses of products CF_3COF and HCOF. The ratio k_1/k_2 was found to be pressure dependent over the range 20–550 Torr but approximately independent of pressure above 700 Torr.

(f) Similar experiments to those of Comment (e) at a total pressure of 740 Torr.

(g) Flash-photolysis time-resolved UV absorption spectroscopic study of CF_3CHFO_2 radicals from F_2-CF_3CH_2F-O_2-N_2 mixtures, k_1 obtained from a fit of CF_3O_2 formation profiles, produced from reaction (1) followed by $CF_3 + O_2 + M \rightarrow CF_3O_2 + M$. Experiments were carried out at a total pressure of 230 Torr, well below the high-pressure limit.

(h) Cl_2-initiated photooxidation of CF_3CH_2F at 1 atm pressure, with dual-beam diode-array UV spectroscopic determination of CF_3COF and HCOF products.

(i) Steady-state photolyses of Cl_2 in the presence of CF_3CHF_2-air mixtures (1 atm) with FTIR absorption spectroscopic analyses; a 109±5% yield of COF_2 was observed, consistent with $k_1[O_2] \ll k_2$.

(j) Similar experiments to those of comment (i) at a total pressure of 740 Torr; a ~100% yield of COF_2 was observed, consistent with $k_1[O_2] \ll k_2$.

(k) Steady-state photolysis of Cl_2 in the presence of CH_2FCl-air mixtures (740 Torr) with FTIR absorption spectroscopic analyses; a 100% yield of HCOF was observed, consistent with $k_1[O_2] \ll k_2$.

(l) Steady-state photolyses of Cl_2 in the presence of CH_2FCl-air mixtures (700 Torr) with FTIR absorption spectroscopic analysis; a 111±6% yield of COF_2 was observed, consistent with $k_1[O_2] \ll k_2$.

(m) Similar experiments to those of Comment (l) at a total pressure of 740 Torr; a 100% yield of COF_2 was observed, consistent with $k_1[O_2] \ll k_2$.

(n) Steady-state photolysis of Cl_2 in the presence of $CHFCl_2$-air mixtures (740 Torr) with FTIR absorption spectroscopic analyses; a 100% yield of COFCl was observed, consistent with $k_1[O_2] \ll k_2$.

(o) Steady-state photolyses of Cl_2 in the presence of CH_3CF_2Cl-air mixtures (740 Torr) with FTIR spectroscopic analysis. A 100% yield of CF_2ClCHO was observed, consistent with $k_1[O_2] \gg k_2$. Experiments on this reaction were also carried out by Edney and Driscoll[1] and Tuazon and Atkinson.[2]

(p) Steady-state photolysis of Cl_2 in the presence of CH_3CFCl_2-air mixtures (740 Torr) with FTIR analysis; a 100% yield of $CFCl_2CHO$ was observed, consistent with $k_1[O_2] \gg k_2$. Experiments on this system were also carried out by Tuazon and Atkinson[1] and Edney *et al.*[9]

(q) Steady-state photolyses of Cl_2 in the presence of CF_3CHFCl-air mixtures (1 atm) with FTIR absorption spectroscopic analyses; a 100±4% yield of CF_3COF was observed, consistent with $k_1[O_2] \ll k_2$.

(r) Steady-state photolysis of Cl_2 in the presence of CF_3CHFCl-air mixtures at 740 Torr total pressure with FTIR absorption spectroscopic analyses; a 101±1% yield of CF_3COF was observed, consistent with $k_2 \gg k_1[O_2]$.

(s) Steady-state photolyses of Cl_2 in the presence of CF_3CHCl_2-air mixtures (700 Torr) with FTIR absorption spectroscopic analysis; a ~100% yield of CF_3COCl was observed, consistent with $k_1[O_2] \ll k_2$.

(t) Similar experiments to those of Comment (s) at a total pressure of 100 Torr. The observed formation of CF_3COCl is consistent with $k_1[O_2] \ll k_2$.

(u) Similar experiments to those of Comment (s) at a total pressure of 740 Torr; a 98% yield of CF_3COCl was observed, consistent with $k_1[O_2] \ll k_2$.

(v) Steady-state photolysis of Cl_2 in the presence of CF_3CHCl_2-air mixtures (~1 atm) with broad-band UV absorption analysis; a ~100% yield of CF_3COCl was observed, consistent with $k_1[O_2] \ll k_2$.

(w) Steady-state photolysis of Cl_2 in the presence of $CF_3CF_2CHCl_2$-O_2 mixtures (100 Torr) with FTIR spectroscopic analysis; observed formation of CF_3CF_2COCl is consistent with $k_1[O_2] \ll k_2$.

(x) Steady-state photolysis of Cl_2 in the presence of $CF_3CF_2CHCl_2$-air mixtures (740 Torr) with FTIR spectroscopic analysis; a 100% yield of CF_3CF_2COCl was observed, consistent with $k_1[O_2] \ll k_2$.

(y) Steady-state photolysis of Cl_2 in the presence of CF_2ClCF_2CHFCl-O_2 mixtures (100 Torr) with FTIR spectroscopic analysis; observed formation of CF_2ClCF_2COF is consistent with $k_1[O_2] \ll k_2$.

(z) Steady-state photolysis of Cl_2 in the presence of CF_2ClCF_2CHFCl-air mixtures (740 Torr) with FTIR spectroscopic analysis; a 99% yield of CF_2ClCF_2COF was observed, consistent with $k_1[O_2] \ll k_2$.

(aa) Steady-state photolysis of Cl_2 in the presence of CH_3Cl-O_2-N_2 mixtures with FTIR spectroscopic analysis of HOCl, CO, HCl, and $CH_2ClCOOH$ products. k_1/k_2 based on yields of CO and HOCl, the latter being corrected for secondary formation and removal. The ratio k_1/k_2 was found to be markedly pressure dependent over the range 12 to 700 Torr, and the cited value refers to 700 Torr total pressure.

(bb) Steady-state photolysis of Cl_2 in the presence of C_2H_5Cl-O_2-N_2 mixture with FTIR spectroscopic analysis of products; the observed high yields of HCl (157%) and CO_2 (53%) were explained by reaction (2).

(cc) Laser flash photolyses of Cl_2 in the presence of C_2H_5Cl-air mixtures with transient infrared absorption detection of HCl. The observed secondary formation of HCl was explained by reaction (2).

(dd) Steady-state photolysis of CH_3ONO or C_2H_5ONO in the presence of chloroethene-NO-air mixtures, with and without C_2H_6 as an added Cl atom scavenger. FTIR spectroscopic analysis of HCHO and HCOCl products, with close to unit yields of each. These products and their formation yields are consistent with the qualitative relative values of $k_1[O_2]$ and k_2 as shown above.

(ee) Steady-state photolyses of CH_3CCl_3-O_2 mixtures in the presence of Br_2 or NO (to scavenge Cl atoms), with GC and IR analyses of products. CH_3COCl was the major product observed, consistent with the relative values of $k_1[O_2]$ and k_2 shown above.

(ff) Steady-state photolysis of Cl_2 in the presence of CH_3CCl_3-O_2 mixtures with GC and IR analyses of CCl_3CHO and $COCl_2$, which are consistent with the relative values of $k_1[O_2]$ and k_2 shown above.

(gg) Steady-state photolysis of Cl_2 in the presence of $CHCl_2CCl_3$-O_2 mixtures (100 Torr) with FTIR spectroscopic analysis. The observed formation of yields of CCl_3COCl and $COCl_2$ are consistent with the relative values of $k_1[O_2]$ and k_2 shown above.

Preferred Values

$R_1(R_2)CHO = CF_3CHFO$

$k_1/k_2 = 2.7\times10^{-20}$ cm^3 molecule^{-1} at 298 K and 1 atm pressure.

$k_1/k_2 = 1.1\times10^{-25}\exp(3700/T)$ cm^3 molecule^{-1} over the temperature range 260–355 K and 1 bar pressure.

$\Delta(E/R) = \pm500$ K.

$R_1(R_2)CHO = CH_2ClO$

$k_1/k_2 = 4.6\times10^{-18}$ cm^3 molecule^{-1} at 298 K.

Comments on Preferred Values

$R_1(R_2)CHO = CF_3CHFO$

The recommended temperature dependence rate coefficient ratio is that evaluated by Rattigan *et al.*[7] from their own data together with those of Wallington *et al.*,[4] Tuazon and Atkinson,[5] and Maricq and Szente.[6]

$R_1(R_2)CHO = CH_2ClO$

The elimination of HCl occurs from the CH_3CHClO radical[13,14] as well as from the CH_2ClO radical.[12]

$R_1(R_2)CHO$ = other radicals in the above table

For the purposes of atmospheric modeling studies it is recommended that the above qualitative information on the ratios k_1/k_2 be used to decide if one or other of the alkoxy radical reaction pathways predominates or if both pathways should be considered.

References

[1] E. O. Edney and D. J. Driscoll, Int. J. Chem. Kinet. **24**, 1067 (1992).
[2] E. C. Tuazon and R. Atkinson, J. Atmos. Chem. **17**, 179 (1993).
[3] T. J. Wallington, M. D. Hurley, J. C. Ball, T. Ellermann, O. J. Nielsen, and J. Sehested, J. Phys. Chem. **98**, 5435 (1994).
[4] T. J. Wallington, M. D. Hurley, J. C. Ball, and E. W. Kaiser, Environ. Sci. Technol. **26**, 1318 (1992).
[5] E. C. Tuazon and R. Atkinson, J. Atmos. Chem. **16**, 301 (1993).
[6] M. M. Maricq and J. J. Szente, J. Phys. Chem. **96**, 10862 (1992).
[7] O. V. Rattigan, D. M. Rowley, O. Wild, R. L. Jones, and R. A. Cox, J. Chem. Soc. Faraday Trans. **90**, 1819 (1994).
[8] E. C. Tuazon and R. Atkinson, Environ. Sci. Technol. **28**, 2306 (1994).
[9] E. O. Edney, B. W. Gay, and D. J. Driscoll, J. Atmos. Chem. **12**, 105 (1991).
[10] H. Sato and T. Nakamura, J. Chem. Soc. Jpn. **5**, 548 (1991).
[11] G. D. Hayman, M. E. Jenkin, T. P. Murrells, and C. E. Johnson, Atmos. Environ. **28A**, 421 (1994).
[12] E. W. Kaiser and T. J. Wallington, J. Phys. Chem. **98**, 5679 (1994).
[13] J. Shi, T. J. Wallington, and E. W. Kaiser, J. Phys. Chem. **97**, 6184 (1993).
[14] M. M Maricq, J. Shi, J. J. Szente, L. Rimai, and E. W. Kaiser, J. Phys. Chem. **97**, 9686 (1993).
[15] E. C. Tuazon, R. Atkinson, S. M. Aschmann, M. A. Goodman, and A. M. Winer, Int. J. Chem. Kinet. **20**, 241 (1988).
[16] L. Nelson, I. Shanahan, H. W. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 577 (1990).

$RO_2 + NO \rightarrow RO + NO_2$ (1)

($R = CH_2F, CHF_2, CF_3, CH_2FCHF, CHF_2CF_2, CF_3CHF, CF_3CF_2, CF_2Cl, CFCl_2, CF_2ClCH_2, CFCl_2CH_2, CF_3CCl_2, CH_2Cl, CCl_3, CH_2Br$)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$R = CH_2F$ $(1.25\pm0.13)\times10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993[1]	(a)
$R = CHF_2$ $(1.26\pm0.16)\times10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993[1]	(a)
$R = CF_3$ $(1.78\pm0.36)\times10^{-11}$	295	Plumb and Ryan, 1982[2]	(b)
1.45×10^{-11} $(T/298)^{-(1.2\pm0.2)}$	230–430	Dognon, Caralp, and Lesclaux, 1985[3]	(c)
$(1.45\pm0.2)\times10^{-11}$	298		
$(1.53\pm0.30)\times10^{-11}$	290	Peeters, Vertommen, and Langhans, 1992[4]	(d)
$(1.68\pm0.26)\times10^{-11}$	295	Sehested and Nielsen, 1993[5]	(a)
$(1.53\pm0.20)\times10^{-11}$	297	Bevilacqua, Hanson, and Howard, 1993[6]	(e)
$(1.57\pm0.38)\times10^{-11}$	298	Turnipseed, Barone, and Ravishankara, 1994[7]	(f)
$R = CH_2FCHF$ $>8.7\times10^{-12}$	296	Wallington *et al.*, 1994[8]	(a)
$R = CHF_2CF_2$ $>(9.7\pm1.3)\times10^{-12}$	295	Sehested, Nielsen, and Wallington, 1993[1]	(a)
$R = CF_3CHF$ $(1.28\pm0.36)\times10^{-11}$	298	Wallington and Nielsen, 1991[9]	(a)
$R = CF_3CF_2$ $>(1.07\pm0.15)\times10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993[1]	(a)
$R = CF_2Cl$ $1.6\times10^{-11}(T/298)^{-(1.5\pm0.4)}$	230–430	Dognon, Caralp, and Lesclaux, 1985[3]	(c)
$(1.6\pm0.3)\times10^{-11}$	298		
$(1.31\pm0.12)\times10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993[1]	(a)
$R = CFCl_2$ $(1.6\pm0.2)\times10^{-11}$	298	Lesclaux and Caralp, 1984[10]	(g)
$1.45\times10^{-11}(T/298)^{-(1.3\pm0.2)}$	230–430	Dognon, Caralp, and Lesclaux, 1985[3]	(c)
$(1.45\pm0.2)\times10^{-11}$	298		
$R = CF_2ClCH_2$ $(1.18\pm0.10)\times10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993[1]	(a)
$R = CFCl_2CH_2$ $(1.28\pm0.11)\times10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993[1]	(a)
$R = CF_3CCl_2$ $(1.5–2.0)\times10^{-11}$	298	Hayman *et al.*, 1994[11]	(h)
$R = CH_2Cl$ $(1.87\pm0.20)\times10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993[1]	(a)
$R = CCl_3$ $(1.86\pm0.28)\times10^{-11}$	295	Ryan and Plumb, 1984[12]	(i)
$1.7\times10^{-11}(T/298)^{-(1.0\pm0.2)}$	230–430	Dognon, Caralp, and Lesclaux, 1985[3]	(c)
$(1.7\pm0.2)\times10^{-11}$	298		
$R = CH_2Br$ $(1.07\pm0.11)\times10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993[1]	(a)
Reviews and Evaluations			
$R = CF_3$ $1.6\times10^{-11}(T/300)^{-1.2}$	230–430	IUPAC, 1992[13]	(j)
$5.4\times10^{-12}\exp[(320\pm150)/T]$	230–430	NASA, 1994[14]	(k)
$1.6\times10^{-11}(T/298)^{-1.2}$	228–433	Lightfoot *et al.*, 1992[15]	(l)
$1.45\times10^{-11}(T/298)^{-1.2}$	230–430	Wallington *et al.*, 1992[16]	(l)
$R = CF_3CHF$ 1.28×10^{-11}	298	Lightfoot *et al.*, 1992[15]	(m)

Rate coefficient data—Continued

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
R = CF_2Cl $1.6\times10^{-11}(T/300)^{-1.5}$	230–430	IUPAC, 1992[13]	(l)
3.8×10^{-12} exp[(400±200)/T]	230–430	NASA, 1992[14]	(n)
$1.6\times10^{-11}(T/298)^{-1.5}$	228–413	Lightfoot *et al.*, 1992[15]	(l)
$1.6\times10^{-11}(T/298)^{-1.5}$	230–430	Wallington *et al.*, 1992[16]	(l)
R = $CFCl_2$ $1.5\times10^{-11}(T/300)^{-1.3}$	230–430	IUPAC, 1992[13]	(l)
4.5×10^{-12} exp[(350±200)/T]	230–430	NASA, 1992[14]	(l)
$1.5\times10^{-11}(T/298)^{-1.3}$	228–413	Lightfoot *et al.*, 1992[15]	(l)
$1.45\times10^{-11}(T/298)^{-1.3}$	230–430	Wallington *et al.*, 1992[16]	(l)
R = CCl_3 $1.8\times10^{-11}(T/300)^{-1.0}$	230–430	IUPAC, 1992[13]	(j)
5.7×10^{-12} exp[(330±200)/T]	230–430	NASA, 1992[14]	(j)
$1.8\times10^{-11}(T/298)^{-1.0}$	229–413	Lightfoot *et al.*, 1992[15]	(l)
$1.7\times10^{-11}(T/298)^{-1.0}$	230–430	Wallington *et al.*, 1992[16]	(l)

Comments

(a) Pulse-radiolysis combined with time-resolved UV-VIS absorption spectroscopy; k determined from $+d[NO_2]/dt$ at a total pressure of 1 bar.
(b) Discharge flow-mass spectrometry system used. The rate coefficient was independent of pressure over the range 1.9–5.1 Torr.
(c) Pulsed laser photolysis-mass spectrometry system used. No significant pressure dependence of the rate coefficient over the range 1–10 Torr was observed.
(d) Fast-flow system with molecular beam sampling MS at total pressures of 2 Torr; k was derived from decay of CF_3O_2 and appearance of NO_2.
(e) Flow tube reactor coupled to chemical ionization MS. k determined from decay of CF_3O_2 in the presence of NO; pressure range 0.8–2 Torr.
(f) Pulsed laser photolysis of CF_3Br in the presence of O_2 and NO at 70 Torr total pressure. CF_3O radicals were detected by LIF and the rate coefficient k was obtained by fitting the measured CF_3O radical temporal profile, with formation through CF_3O_2 + NO and loss through CF_3O + NO.
(g) Pulsed laser photolysis-mass spectrometry system used. Measurements were made at 2 Torr total pressure.
(h) Laser flash photolysis system with time-resolved UV absorption spectroscopy for $CF_3CCl_2O_2$ radicals at a total pressure of 1 atm. k derived from computer fit of transient absorption traces based on a mechanism of 9 reactions.
(i) Discharge flow-mass spectrometry system used. The rate coefficient was independent of pressure over the range 1.7–5.4 Torr.
(j) Based on the rate coefficients of Plumb and Ryan[2,12] and Dognon *et al.*[3]
(k) Based on the rate coefficients of Plumb and Ryan,[2] Dognon *et al.*,[3] Peeters *et al.*,[4] Sehested and Nielsen,[5] Bevilacqua *et al.*,[6] and Turnipseed *et al.*[7]
(l) Recommendation based on the results of Dognon *et al.*[3]
(m) Recommendation based on the results of Wallington and Nielsen.[9]
(n) Based on the rate coefficients of Dognon *et al.*[3] and Sehested *et al.*[1]

Preferred Values

R = CH_2F
$k=1.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta\log k=\pm0.3$ at 298 K.
R = CHF_2
$k=1.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta\log k=\pm0.3$ at 298 K.
R = CF_3
$k=1.6\times10^{-11}\ (T/298)^{-1.2}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–430 K.
$\Delta\log k=\pm0.15$ over the temperature range 230–430 K.
R = CH_2FCHF
$k>9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
R = CHF_2CF_2
$k>1\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
R = CF_3CHF
$k=1.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta\log k=\pm0.3$ at 298 K.
R = CF_3CF_2
$k>1\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
R = CF_2Cl
$k=1.5\times10^{-11}\ (T/298)^{-1.5}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–430 K.
$\Delta\log k=\pm0.2$ over the temperature range 230–430 K.
R = $CFCl_2$
$k=1.5\times10^{-11}\ (T/298)^{-1.3}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–430 K.
$\Delta\log k=\pm0.2$ over the temperature range 230–430 K.
R = CF_2ClCH_2
$k=1.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta\log k=\pm0.3$ at 298 K.
R = $CFCl_2CH_2$
$k=1.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta\log k=\pm0.3$ at 298 K.
R = CF_3CCl_2
$k=1.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta\log k=\pm0.3$ at 298 K.
R = CH_2Cl
$k = 1.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta\log k=\pm0.3$ at 298 K.
R = CCl_3
$k=1.8\times10^{-11}\ (T/298)^{-1.0}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–430 K.
$\Delta\log k=\pm0.2$ over the temperature range 230–430 K.
R = CH_2Br
$k = 1.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta\log k=\pm0.3$ at 298 K.

Comments on Preferred Values

R=CH_2F, CHF_2, CHF_2CF_2, CF_3CF_2, CF_2ClCH_2, $CFCl_2CH_2$, CH_2Cl, CH_2Br

The preferred values are the rounded-off rate coefficients determined by Sehested *et al.*[1]

R = CF_3

The preferred values are based on the temperature dependent data of Dognon *et al.*,[3] adjusted to fit the average value of k_{298} from the data of Plumb and Ryan,[2] Dognon *et al.*,[3] Peeters *et al.*,[4] Sehested and Nielsen,[5] Bevilacqua *et al.*,[6] and Turnipseed *et al.*[7]

R = CH_2FCHF

The preferred value is the rounded-off lower limit of Wallington *et al.*[8]

R = CF_3CHF

The preferred value is the rounded-off rate coefficient determined by Wallington and Nielsen.[9]

R = CF_2Cl

The preferred values are based on the temperature dependent data of Dognon *et al.*[3] adjusted to fit the average value of k_{298} from the data of Sehested *et al.*[1] and Dognon *et al.*[3]

R = $CFCl_2$

The preferred values are based on the temperature dependent data of Dognon *et al.*,[3] adjusted to fit the average value of k_{298} from the data of Lesclaux and Caralp[10] and Dognon *et al.*[3]

R = CF_3CCl_2

The preferred value is the mid-point of the range of values determined by Hayman *et al.*[11]

R = CCl_3

The preferred values are based on the temperature dependent data of Dognon *et al.*,[3] adjusted to fit the average value of k_{298} from the data of Ryan and Plumb[12] and Dognon *et al.*[3]

The temperature dependence expressions are given in the form favored by Dognon *et al.*,[3] which best describe the measured data. If Arrhenius expressions are required, then the expressions recommended by NASA, 1994[14] should be employed. In view of the consistent observation of pressure independence, it seems unlikely that $RONO_2$ is produced as a product. Dognon *et al.*[3] measured quantum yields for NO_2 greater than unity for all the RO_2 radicals studied; suggesting that the RO_2 + NO reactions form RO and NO_2 exclusively, with additional NO_2 being produced from secondary chemistry.

References

[1] J. Sehested, O. J. Nielsen, and T. J. Wallington, Chem. Phys. Lett. **213**, 457 (1993).
[2] I. C. Plumb and K. R. Ryan, Chem. Phys. Lett. **92**, 236 (1982).
[3] A. M. Dognon, F. Caralp, and R. Lesclaux, J. Chim. Phys. **82**, 349 (1985).
[4] J. Peeters, J. Vertommen, and I. Langhans, Ber. Bunsenges. Phys. Chem. **96**, 431 (1992).
[5] J. Sehested and O. J. Nielsen, Chem. Phys. Lett. **206**, 369 (1993).
[6] T. J. Bevilacqua, D. R. Hanson, and C. J. Howard, J. Phys. Chem. **97**, 3750 (1993).
[7] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **98**, 4594 (1994).
[8] T. J. Wallington, M. D. Hurley, J. C. Ball, T. Ellermann, O. J. Nielsen, and J. Sehested, J. Phys. Chem. **98**, 5435 (1994).
[9] T. J. Wallington and O. J. Nielsen, Chem. Phys. Lett. **187**, 33 (1991).
[10] R. Lesclaux and F. Caralp, Int. J. Chem. Kinet. **16**, 1117 (1984).
[11] G. D. Hayman, M. E. Jenkin, T. P. Murrells, and C. E. Johnson, Atmos. Environ. **28A**, 421 (1994).
[12] K. R. Ryan and I. C. Plumb, Int. J. Chem. Kinet. **16**, 591 (1984).
[13] IUPAC, Supplement IV, 1992 (see references in Introduction).
[14] NASA Evaluation No. 11, 1994 (see references in Introduction).
[15] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).
[16] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).

$CF_3O_2 + O_3 \rightarrow CF_3O + 2O_2$

$\Delta H^\circ = -184.3\ kJ\cdot mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<5\times10^{-15}$	295	Nielsen and Sehested, 1993[1]	(a)
$<1\times10^{-14}$	210–353	Maricq and Szente, 1993[2]	(b)
$<3\times10^{-15}$	298	Ravishankara *et al.*, 1994[3]	(c)
$<7\times10^{-15}$	298	Turnipseed, Barone, and Ravishankara, 1994[4]	(d)
Reviews and Evaluations			
$<3\times10^{-15}$	298	NASA, 1994[5]	(e)

Comments

(a) Pulse radiolysis/UV absorption technique. Radicals were generated by pulse radiolysis of CHF_3-O_2-O_3-SF_6 mixtures. Upper limit for k derived from simulations of ozone absorption transients at 254 nm and 276 nm in the presence of CF_3O and CF_3O_2.

(b) Flash photolysis/UV absorption technique. Radicals were generated by 351 nm photolysis of F_2 in a flowing F_2-CHF_3-O_3-O_2-N_2 mixture. O_3 and CF_3O_2 radicals were monitored by absorption at 255 nm and 210 nm, respectively.

(c) Flow tube reactor/chemical ionization mass spectrometer technique. CF_3O_2 radicals were generated by pyrolysis of CF_3I in the presence of O_2.

(d) Pulsed laser photolysis/pulsed laser-induced fluorescence technique. CF_3O_2 radicals were generated by photolysis of CF_3Br-O_2-NO mixtures.

(e) Based on the results of Ravishankara *et al.*[3]

Preferred Values

$k<3\times10^{-15}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

Comments on Preferred Values

This evaluation accepts the recommendation of the NASA Panel for Data Evaluation.[5] The preferred upper limit at 298 K is based on the results of Ravishankara *et al.*[3] In that study the temporal profile of CF_3O_2 radicals was measured in a flow tube reactor with chemical ionization mass spectrometry detection of CF_3O_2 in excess O_3. An excess of isobutane was added to scavenge any CF_3O produced and thereby inhibit the possible regeneration of CF_3O_2 by reaction of the product CF_3O with O_3. No measurable reaction was observed. Less sensitive upper limits were reported in the less direct studies of Nielsen and Sehested,[1] Maricq and Szente,[2] and Turnipseed *et al.*[4]

References

[1] O. J. Nielsen and J. Sehested, Chem. Phys. Lett. **213**, 433 (1993).

[2] M. M. Maricq and J. J. Szente, Chem. Phys. Lett. **213**, 449 (1993).

[3] A. R. Ravishankara, A. A. Turnipseed, N. R. Jensen, S. Barone, M. Mills, C. J. Howard, and S. Solomon, Science **263**, 71 (1994).

[4] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **98**, 4594 (1994).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

$CF_3O_2 + NO_2 + M \rightarrow CF_3O_2NO_2 + M$

$\Delta H° = -105$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 4.5 \times 10^{-29}$ $(T/300)^{-6.4}$ $[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values correspond to the theoretical analysis of Ref. 1, which was based on the experiments of Ref. 2. A value of $F_c = 0.28$ at 300 K was calculated and used. In contrast to Ref. 1, however, an adjustment of ΔH_0° to the value of -103.6 kJ mol^{-1} was made in order to meet the trend for formation of other $CX_3O_2NO_2$ (X = Cl, F) which were investigated in Ref. 3. This modifies the k_0 values in the indicated way. Falloff curves correspond to $F_c = 0.28$ at 220–300 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ over the temperature range 200–300 K.

Comments on Preferred Values

See comment to k_0. Because the measurements were made at low pressures only, the extrapolation to k_∞ remains fairly uncertain. F_c was calculated[1] to be close to 0.28 over the temperature range 220–300 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).

[2] F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2, **84**, 569 (1988).

[3] D. Köppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CF_3O_2NO_2 + M \rightarrow CF_3O_2 + NO_2 + M$

$\Delta H° = 105$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 3.6 \times 10^{-19}$ [N_2] s^{-1} at 298 K.

$k_0 = 5 \times 10^{-1}$ $(T/300)^{-6}$ $\exp(-12460/T)$ [N_2] s^{-1} over the temperature range 233–373 K.

Reliability

$\Delta \log k_0 = \pm 0.4$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are from the theoretical analysis of Ref. 1 which is based on measurements of the reverse reaction[2] and calculated equilibrium constants with $\Delta H_0^\circ = 103.6$ kJ mol^{-1}, adjusted to meet the extrapolated value of Ref. 3. $F_c = 0.28$ was calculated[1] for 220–300 K. Direct measurements of the dissociation rate are required together with measurements over a wider pressure range. $F_c = 0.28$ is used for falloff curves over the range 220–300 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 5.6 \times 10^{-2}$ s^{-1} at 298 K.

$k_\infty = 1.2 \times 10^{17}$ $\exp(-12580/T)$ s^{-1} over the temperature range 233–373 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

See comments on k_0. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).

[2] F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2, **84**, 569 (1988).

[3] D. Köppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_2FO_2 + CH_2FO_2 \rightarrow CH_2FOH + HCOF + O_2$ (1)
$\rightarrow 2CH_2FO + O_2$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 3.3 \times 10^{-13} \exp(700/T)$	228–380	Dagaut, Wallington, and Kurylo, 1988[1]	(a,b)
$\leq 3.1 \times 10^{-12}$	298		
$\leq 4.0 \times 10^{-12}$	298	Wallington *et al.*, 1992[2]	(a,c)
Branching Ratios			
$k_2/k > 0.77$	298	Wallington *et al.*, 1992[2]	(d)
Reviews and Evaluations			
$k_{obs} = 3.8 \times 10^{-13} \exp(700/T)$	228–370	Lightfoot *et al.*, 1992[3]	(e)
$k_{obs} = 3.3 \times 10^{-13} \exp(700/T)$	228–380	Wallington, Dagaut, and Kurylo, 1992[4]	(f)

Comments

(a) k is defined by $-d[CH_2FO_2]/dt=2k[CH_2FO_2]^2$ and has been derived from the measured overall second-order decay of CH_2FO_2 radicals (k_{obs}).

(b) Flash photolysis of Cl_2 in the presence of CH_3F-O_2-N_2 mixtures at total pressures of 25–400 Torr. CH_2FO_2 radicals were monitored by UV absorption with $\sigma_{240}=(3.72 \pm 0.45)\times 10^{-18}$ cm^2 molecule^{-1}. The derived value of $k_{obs}=(3.3\pm1.2)\times 10^{-13} \exp[(700 \pm 100)/T]$ cm^3 molecule^{-1} s^{-1} is an upper limit to k, owing to the possibility of secondary reactions producing an enhanced decay of CH_2FO_2 radicals (see Comments on Preferred Values).

(c) Pulse radiolysis study of CH_3F-O_2-SF_6 mixtures at a total pressure of 1000 mbar. CH_2FO_2 radicals were monitored by UV absorption with $\sigma_{240}=(4.11\pm0.67)\times 10^{-18}$ cm^2 molecule^{-1}. The derived value of $k_{obs}=(4.01\pm0.52)\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K is an upper limit to k, owing to the possibility of secondary reactions producing an enhanced decay of CH_2FO_2 radicals (see Comments on Preferred Values).

(d) CH_2FO_2 radicals were generated from the steady-state photolysis of Cl_2-CH_3F mixtures at 700 Torr pressure of air. The decay of CH_3F and the formation of products was monitored by FTIR spectroscopy. No CH_2FOH was observed within the detection limits of the apparatus. Significant amounts of HCOF were observed (86±5%), and in experiments with high conversions CH_2FOOH was observed (11±4%).

(e) Recalculated from the data of Dagaut *et al.*[1] with a revised value of $\sigma_{240}=4.29\times 10^{-18}$ cm^2 molecule^{-1}.

(f) Based on the data of Dagaut *et al.*[1]

Preferred Values

$k=(2.0\text{–}4.0)\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=(2.0\text{–}4.0)\times 10^{-13} \exp(700/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–380 K.

$k_2/k>0.77$ at 298 K.

Comments on Preferred Values

We have recommended a range of values for the overall rate coefficient as a function of temperature, based on the data of Dagaut *et al.*[1] and modified by a re-evaluation of $\sigma_{240}(CH_2FO_2)$ by Lightfoot *et al.*[3] The upper limit is the measured value of k_{obs} with no correction for possible secondary CH_2FO_2 removal by HO_2 radicals, and the lower limit is a factor of two less than the upper limit, corresponding to a maximum correction for the HO_2 radical reaction.

The product study of Wallington *et al.*[2] showed no formation of CH_2FOH, suggesting that channel (1) is negligible. The high yields of HCOF indicate the occurrence of the reaction $CH_2FO + O_2 \rightarrow HCOF + HO_2$, while the low yields of CH_2FOOH led Wallington *et al.*[2] to suggest that the rate coefficient for the reaction $CH_2FO_2 + HO_2 \rightarrow$ products is appreciably lower than for other $RO_2 + HO_2 \rightarrow$ reactions or that an alternative channel exists for the reactions. More information is needed on the kinetics and mechanisms of the $CH_2FO_2 + HO_2$ reaction to define k and k_2/k more accurately.

References

[1] P. Dagaut, T. J. Wallington, and M. J. Kurylo, Int. J. Chem. Kinet. **20**, 815 (1988).

[2] T. J. Wallington, J. C. Ball, O. J. Nielsen, and E. Bartkiewicz, J. Phys. Chem. **96**, 1241 (1992).

[3] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).

[4] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).

$CHF_2O_2 + CHF_2O_2 \rightarrow CHF_2OH + COF_2 + O_2$ (1)

$\rightarrow 2CHF_2O + O_2$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 5.0\times 10^{-12}$	298	Nielsen *et al.*, 1992[1]	(a,b)
Branching Ratios			
$k_2/k\approx 1.0$	298	Nielsen *et al.*, 1992[1]	(c)

Comments

(a) k is defined by $-d[CHF_2O_2]/dt=2k[CHF_2O_2]^2$ and has been derived from the measured overall second-order decay of CHF_2O_2 radicals (k_{obs}).

(b) Pulse radiolysis study of CH_2F_2-O_2-SF_6 mixtures at a total pressure of 1000 mbar. CHF_2O_2 radicals were monitored by UV absorption with $\sigma_{240}=(2.66\pm0.46)\times10^{-18}$ cm^2 molecule^{-1}. The reported value of $k_{obs}=(5.0\pm0.7)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K is an upper limit to k, because of the possibility of secondary reactions producing an enhanced decay of CHF_2O_2 radicals (see Comments on Preferred Values).

(c) CHF_2O_2 radicals were generated from the steady-state photolysis of Cl_2-CH_2F_2 mixtures in the presence of air at a total pressure of 920 mbar. The decay of CH_2F_2 and the formation of COF_2 were monitored by FTIR spectroscopy. The yield of COF_2 was $104\pm2\%$ of the removal of CH_2F_2.

Preferred Values

$k=(2.5-5)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k\approx1.0$ at 298 K.

Comments on Preferred Values

We have recommended a range of values for the rate coefficient at 298 K, based on the determination by Nielsen *et al.*[1] The upper limit is the measured value of k_{obs} with no correction for possible secondary CHF_2O_2 removal by HO_2 radicals, and the lower limit is a factor of two less than the upper limit, corresponding to a maximum correction for the HO_2 radical reaction.

The product study in the same paper[1] showed that the only carbon-containing product was COF_2, indicating that channel (2) is the predominant, if not the only, pathway, formed followed by the reaction $CHF_2O + O_2 \rightarrow COF_2 + HO_2$. The absence of the product CHF_2OOH expected from the reaction $CHF_2O_2 + HO_2 \rightarrow CHF_2OOH + O_2$, raises several possibilities, including a slow reaction between CHF_2O_2 and HO_2 radicals or an alternative reaction pathway, such as $CHF_2O_2 + HO_2 \rightarrow COF_2 + H_2O + O_2$. More information is needed on the kinetics and mechanism of the $CHF_2O_2 + HO_2$ reaction to define k and k_2/k more accurately.

References

[1] O. J. Nielsen, T. Ellermann, E. Bartkiewicz, T. J. Wallington, and M. D. Hurley, Chem. Phys. Lett. **192**, 82 (1992).

$$\begin{aligned} CF_3O_2 + CF_3O_2 &\rightarrow CF_3OOCF_3 + O_2 \quad (1)\\ &\rightarrow 2CF_3O + O_2 \quad (2)\end{aligned}$$

$\Delta H^\circ(2)=-83.2$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_2=(1.8\pm0.5)\times10^{-12}$	298	Nielsen *et al.*, 1992[1]	(a,b)
$k_2=1.8\times10^{-12}$	298	Maricq and Szente, 1992[2]	(a,c)
$k_2=(1.8\pm0.5)\times10^{-12}$	297	Maricq and Szente, 1992[3]	(a,d)
Branching Ratios			
$k_2/k\approx1.0$	298	Nielsen *et al.*, 1992[1]	(e)

Comments

(a) k is defined by $-d[CF_3O_2]/dt=2k[CF_3O_2]^2$ and has been derived from the measured overall second-order decay of CF_3O_2 radicals (k_{obs}) by correcting for secondary removal of CF_3O_2 radicals.

(b) Pulse radiolysis study of CHF_3-O_2-SF_6 mixtures at a total pressure of 1000 mbar. CF_3O_2 radicals were monitored by UV absorption with $\sigma_{230}=(2.06\pm0.40)\times10^{-18}$ cm^2 molecule^{-1}. The cited rate coefficient was derived by the authors from the observed rate coefficient, $k_{obs}=(3.6\pm0.9)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, on the basis of their product studies [see Comment (e)].

(c) Flash photolysis of CHF_3-F_2-O_2 mixtures with time-resolved absorption spectroscopy for the detection of CF_3O_2 radicals, with $\sigma_{210}=(4.3\pm0.3)\times10^{-18}$ cm^{-2} molecule^{-1}. A value of $k_{obs}=(3.1\pm0.25)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} was determined from the time-dependence of the CF_3O_2 radical absorbance.

(d) Flash photolysis of F_2 in the presence of N_2, O_2, He, and CF_3CFH_2. CF_3O_2 radicals were produced from the reaction $CF_3CHFO \rightarrow CF_3 + HCOF$, followed by $CF_3 + O_2 + M \rightarrow CF_3O_2 + M$, and monitored by UV absorption. A value of $k_{obs}=3.1\times10^{-12}$ cm^3 molecule^{-1} s^{-1} was derived from the rate of disappearance of CF_3O_2 radicals. The value of k_2 quoted above is based on a correction factor of 0.5 to allow for the secondary removal of CF_3O_2 radicals.

(e) CF_3O_2 radicals were generated from the steady-state photolysis of F_2 in the presence of CHF_3-O_2-N_2 mixtures at a total pressure of 892 mbar. The decay of CHF_3 and the formation of products were monitored by FTIR spectroscopy. The major product was CF_3OOOCF_3, which accounted for ~100% of the CHF_3 consumed. No CF_3OOCF_3 was observed as a product. The cited branching ratio was obtained assuming that the trioxide product arises from the reaction $CF_3O + CF_3O_2 + M \rightarrow CF_3OOOCF_3 + M$.

Preferred Values

$k_2 = 1.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_2 = \pm 0.2$ at 298 K.

Comments on Preferred Values

The recommended value of k_2 is obtained by taking the average value of $k_{obs} = 3.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} from the three studies of this reaction[1-3] and by assuming a correction factor of 0.5 to allow for the secondary removal of CF_3O_2 radicals.[1] This correction factor is based on the product study of Nielsen *et al.*,[1] which showed that the sole product of the interaction of CF_3O_2 radicals is the trioxide, CF_3OOOCF_3, which appears to be formed by the reaction $CF_3O + CF_3O_2 + M \rightarrow CF_3OOOCF_3 + M$. The absence of any CF_3OOCF_3 product rules out the participation of channel (1).

References

[1] O. J. Nielsen, T. Ellermann, J. Sehested, E. Bartkiewiecz, T. J. Wallington, and M. D. Hurley, Int. J. Chem. Kinet. **24**, 1009 (1992).

[2] M. M. Maricq and J. J. Szente, J. Phys. Chem. **96**, 4925 (1992).

[3] M. M. Maricq and J. J. Szente, J. Phys. Chem. **96**, 10862 (1992).

$$\begin{aligned} CF_3O_2 + CF_3CHFO_2 &\rightarrow CF_3OOCHFCF_3 + O_2 \quad (1) \\ &\rightarrow CF_3O + CF_3CHFO + O_2 \quad (2) \end{aligned}$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8 \pm 3) \times 10^{-12}$	297	Maricq and Szente, 1992[1]	(a)

Comments

(a) Flash photolysis of F_2 in the presence of CF_3CH_2F-O_2-N_2-He mixtures. CF_3CHFO_2 radicals were monitored by UV absorption with $\sigma_{213} = (5.2 \pm 0.3) \times 10^{-18}$ cm^2 molecule^{-1}. The derived value of k listed above was obtained by modeling the decay of CF_3CFHO_2 radicals and the formation and decay of CF_3O_2 radicals.

Preferred Values

$k = 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K seems reasonable, but requires independent confirmation. Maricq and Szente[1] assumed that the reaction proceeds entirely by channel (2) on the basis of studies of the self-reactions of CF_3O_2 and CF_3CHFO_2 radicals.

References

[1] M. M. Maricq and J. J. Szente, J. Phys. Chem. **96**, 10862 (1992).

$$\mathrm{CHF_2CF_2O_2 + CHF_2CF_2O_2 \rightarrow CHF_2CF_2OOCF_2CHF_2 + O_2} \quad (1)$$
$$\mathrm{\rightarrow 2CHF_2CF_2O + O_2} \quad (2)$$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 2.7\times10^{-12}$	298	Nielsen *et al.*, 1992[1]	(a,b)
Branching Ratios			
$k_2/k\approx1.0$	298	Nielsen *et al.*, 1992[1]	(c)

Comments

(a) k is defined by $-d[\mathrm{CHF_2CF_2O_2}]/dt=2k[\mathrm{CHF_2CF_2O_2}]^2$ and has been derived from the measured overall second-order decay of $\mathrm{CHF_2CF_2O_2}$ radicals (k_{obs}).

(b) Pulse radiolysis study of $\mathrm{CHF_2CHF_2}$-$\mathrm{O_2}$-$\mathrm{SF_6}$ mixtures at a total pressure of 1000 mbar. $\mathrm{CHF_2CF_2O_2}$ radicals were monitored by UV absorption with $\sigma_{230}=(3.2\pm0.5)\times10^{-18}$ cm^2 molecule^{-1}. The reported value of $k_{\mathrm{obs}}=(2.7\pm0.6)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} is an upper limit to k, because of the possibility of secondary reactions producing an enhanced decay of $\mathrm{CHF_2CF_2O_2}$ radicals (see Comments on Preferred Values).

(c) $\mathrm{CHF_2CF_2O_2}$ radicals were generated from the steady-state photolysis of $\mathrm{Cl_2}$ in the presence of $\mathrm{CHF_2CHF_2}$-air mixtures at 920 mbar total pressure. The decay of $\mathrm{CHF_2CHF_2}$ and the formation of $\mathrm{COF_2}$, the only carbon-containing product observed, were monitored by FTIR spectroscopy. The branching ratio given in the table is based on a yield of 98±2% of $\mathrm{COF_2}$, relative to the decay of $\mathrm{CHF_2CHF_2}$.

Preferred Values

$k \leq 3\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k \approx 1.0$ at 298 K.

Comments on Preferred Values

We have recommended an upper limit for the rate coefficient, as determined by Nielsen *et al.*[1] The product study in the same paper[1] revealed that the only carbon-containing product was $\mathrm{COF_2}$, which is assumed to arise from channel (2) followed by the rapid decomposition reaction, $\mathrm{CHF_2CF_2O \rightarrow CHF_2 + COF_2}$. The absence of any peroxide product, $\mathrm{CHF_2CF_2OOCF_2CHF_2}$, together with the carbon balance between the $\mathrm{COF_2}$ produced and the $\mathrm{CHF_2CHF_2}$ consumed indicates that the major, if not the only, pathway for the interaction of the $\mathrm{CHF_2CF_2O_2}$ radicals is via reaction (2). The $\mathrm{CHF_2}$ radicals from the decomposition reaction of the $\mathrm{CHF_2CF_2O}$ reaction will result in the formation of $\mathrm{CHF_2O_2}$ radicals, which are known[2] to interact via the reaction of $\mathrm{2CHF_2O_2 \rightarrow 2CHF_2O + O_2}$, resulting in the formation of $\mathrm{COF_2}$ and $\mathrm{HO_2}$ from the subsequent reaction $\mathrm{CHF_2O + O_2 \rightarrow COF_2 + HO_2}$.

The formation of the peroxy radicals, $\mathrm{CHF_2O_2}$ and $\mathrm{HO_2}$, following the interaction of the initial $\mathrm{CHF_2CF_2O}$ radicals leads to complications in the interpretation of the UV absorption spectra, which were assumed to be exclusively from the $\mathrm{CHF_2CF_2O_2}$ radicals. In the absence of detailed kinetic data concerning the interaction of these peroxy radicals it is not possible to correct the UV absorption spectra. This means that k_{obs} corresponds to an upper limit value of k_2.

References

[1] O. J. Nielsen, T. Ellermann, J. Sehested, and T. J. Wallington, J. Phys. Chem. **96**, 10875 (1992).

[2] O. J. Nielsen, T. Ellermann, E. Bartkiewicz, T. J. Wallington, and M. D. Hurley, Chem. Phys. Lett. **192**, 82 (1992).

$$CF_3CHFO_2 + CF_3CHFO_2 \rightarrow CF_3COF + CF_3CHFOH + O_2 \quad (1)$$

$$\rightarrow 2CF_3CHFO + O_2 \quad (2)$$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
7.8×10^{-13} exp[$(605\pm40)/T$]	211–372	Maricq and Szente, 1992[1]	(a,b)
$(7\pm1.0)\times10^{-12}$	297		
Branching Ratios			
$k_1/k=0.14$	273	Wallington *et al.*, 1992[2]	(c)
$k_1/k=0.08$	298		
$k_1/k=0.05$	353		
$k_1/k=0.055$	273	Tuazon and Atkinson, 1993[3]	(d)
$k_1/k=0.049$	298		
$k_1/k=0.046$	320		

Comments

(a) k is defined by $-d[CF_3CFHO_2]/dt=2k[CF_3CFHO_2]$.[2]

(b) Flash photolysis of F_2 in the presence of N_2, O_2, He, and CF_3CH_2F. CF_3CHFO_2 radicals were monitored by UV absorption with $\sigma_{213}=(5.2\pm0.3)\times10^{-13}$ cm^2 molecule^{-1}. The derived value of k listed above was obtained by modelling the decay curves for CF_3CFHO_2 radicals with a mechanism of 9 reactions.

(c) Steady-state photolysis of Cl_2 in the presence of CF_3CFH_2-O_2 mixtures at a total pressure of 1000 Torr with FTIR analysis of the products HCOF and CF_3COF. The branching ratio was determined from the yields of CF_3COF as a function of added O_2, extrapolated to zero O_2 partial pressure.

(d) Similar experiments to those of Comment (c). The branching ratios were derived from the yields of CF_3COF in the presence of 590 Torr N_2 and 1 Torr O_2.

Preferred Values

$k=5.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=7.8\times10^{-13}\exp(605/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210–375 K.

$k_2/k=0.93$, independent of temperature over the range 270–350 K.

$k_1/k=0.07$, independent of temperature over the range 270–350 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

$\Delta(E/R)=\pm200$ K.

$\Delta(k_1/k)=\Delta(k_2/k)=\pm0.05$ over the temperature range 270–350 K.

Comments on Preferred Values

The preferred data for the overall rate coefficient are from Maricq and Szente,[1] which are based on temperature-independent branching ratios k_1/k and k_2/k over the range 273–363 K. This is consistent with our recommendation of a temperature-independent branching ratio, k_1/k, which is the average of the experimental results of Wallington *et al.*[2] and Tuazon and Atkinson[3] over the range 273–353 K. The recommended value of k_2/k is inferred from that of k_1/k.

It should also be noted that the results of Maricq and Szente[1] for k at 216 K appear consistent with temperature-independent branching ratios.

Confirmation of both the overall rate coefficient and the branching ratios is required.

References

[1] M. M. Maricq and J. J. Szente, J. Phys. Chem. **96**, 10862 (1992).
[2] T. J. Wallington, M. D. Hurley, J. C. Ball, and E. W. Kaiser, Environ. Sci. Technol. **26**, 1318 (1992).
[3] E. C. Tuazon and R. Atkinson, J. Atmos. Chem. **16**, 301 (1993).

$CF_3CF_2O_2 + CF_3CF_2O_2 \rightarrow CF_3CF_2OOCF_2CF_3 + O_2$ (1)
$\rightarrow 2CF_3CF_2O + O_2$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 2.1 \times 10^{-12}$	295	Sehested *et al.*, 1993[1]	(a,b)
Branching Ratios			
$k_2/k=1.0$	295	Sehested *et al.*, 1993[1]	(c)

Comments

(a) k is defined by $-d[CF_3CF_2O_2]-2k[CF_3CF_2O_2]^2$ and has been derived from the measured overall second-order decay of $CF_3CF_2O_2$ radicals (k_{obs}).

(b) Pulse radiolysis study of CF_3CF_2H-O_2-SF_6 mixtures at a total pressure of 1000 mbar. $CF_3CF_2O_2$ radicals were monitored by UV absorption with $\sigma_{230}=(2.74 \pm 0.46)\times 10^{-18}$ cm^2 molecule^{-1}. The derived value of $k_{obs}=(2.10\pm 0.38)\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is an upper limit to k, because of the possibility of secondary reactions producing an enhanced decay of $CF_3CF_2O_2$ radicals (see Comments on Preferred Values).

(c) $CF_3CF_2O_2$ radicals were generated from the steady-state photolysis of Cl_2-CF_3CF_2H mixtures at 700 Torr pressure of air. The decay of CF_3CF_2H and the formation of products were monitored by FTIR spectroscopy. The observed products were COF_2, $CF_3O_3CF_3$, and $CF_3O_3C_2F_5$, and accounted for 100% of the CF_3CF_2H loss.

Preferred Values

$k_2 \leq 2\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k=1.0$ at 298 K.

Comments on Preferred Values

We have recommended a rounded-off upper limit for the rate coefficient (k_2) as determined by Sehested *et al.*[1] The product study in the same paper[1] showed no formation of the peroxide product, $CF_3CF_2OOCF_2CF_3$, and together with the carbon-balance between the products COF_2, $CF_3O_3CF_3$, $CF_3O_3C_2F_5$, and the decay of CF_3CF_2H indicates that reaction (2) is the sole channel for the interaction of $CF_3CF_2O_2$ radicals. The observed products are accounted for by the reactions of CF_3CF_2O radicals: $CF_3CF_2O \rightarrow CF_3+COF_2$; $CF_3 + O_2 + M \rightarrow CF_3O_2 + M$; $CF_3O_2 + CF_3CF_2O \rightarrow CF_3O_3C_2F_5$; $CF_3O + CF_3O_2 \rightarrow CF_3O_3CF_3$. Because it is not possible at present to correct for the secondary removal of $C_2F_5O_2$ radicals in reactions with CF_3O and probably also with CF_3O_2 radicals, the reported k_{obs} value from the second-order removal of $C_2F_5O_2$ radicals is an upper limit.

References

[1] J. Sehested, T. Ellermann, O. J. Nielsen, T. J. Wallington, and M. D. Hurley, Int. J. Chem. Kinet. 25, 701 (1993).

HCOF + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°/kJ·mol^{-1}	$\lambda_{threshold}$/nm
HCOF + $h\nu \rightarrow$ HF+CO (1)	8.7	13,730
$\rightarrow$ H+FCO (2)	439	272
$\rightarrow$ F+HCO (3)	476	251

Absorption cross-section data

Wavelength range/nm	References	Comments
220–300	Rattigan *et al.*, 1994[1]	(a)
195–270	Meller and Moortgat, 1992[1]	(b)

Comments

(a) The absorption spectrum of HCOF was studied using a purified sample of HCOF and recorded by diode array spectroscopy with a resolution of 1.2 nm. The characteristic banded structure was recorded and the absolute cross-section at 230 nm was $\sigma=6.65\times10^{-20}$ cm^2 molecule^{-1} using this resolution. The cross-section was independent of temperature in the range 233–318 K, in agreement with the earlier work of Giddings and Innes.[3]

(b) Measurements of the spectrum of HCOF at a resolution of 0.02 nm. The spectrum consists of a vibrational progression of many sharp bands, with an origin of structured absorption at 268 nm and a maximum of intensity near 210 nm. The maximum value of $\sigma=1.5\times10^{-19}$ cm^2 molecule^{-1} was observed at this resolution, which is in reasonable agreement with the earlier work of Giddings and Innes[3] who reported an absorption coefficient of approximately 50 l mol^{-1} cm^{-1} ($\sigma=1.9\times10^{-19}$ cm^2 molecule^{-1}) at the maximum.

Quantum yield data

There are no reported quantum yield data. Klimeck and Berry[4] have observed infrared laser emission from HF* following flash photolysis of HCOF ($\lambda>165$ nm). These results[4] indicate the occurrence of reactions (1) and/or (3).

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2
200	8.28	223	6.58	245	0.67
201	9.75	224	4.94	246	0.72
202	8.3	225	5.33	247	0.41
203	7.55	226	4.00	248	0.48
204	8.52	227	4.65	249	0.28
205	10.15	228	4.43	250	0.21
206	8.28	229	4.61	251	0.15
207	7.41	230	3.57	252	0.24
208	8.44	231	2.55	253	0.21
209	9.55	232	3.16	254	0.07
210	7.76	233	3.09	255	0.12
211	7.36	234	2.98	256	0.07
212	7.92	235	2.04	257	0.05
213	8.56	236	2.28	258	0.04
214	9.22	237	1.24	259	0.04
215	7.67	238	1.71	260	0.04
216	6.51	239	1.75	261	0.02
217	7.38	240	1.55	262	0.02
218	7.97	241	0.97	263	0.02
219	6.28	242	1.19	264	0.02
220	6.85	243	0.57	265	0.01
221	5.7	244	0.76	266	0.01
222	6.07				

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data for the absolute absorption cross-sections reported by Meller and Moortgat.[2] The listed values are averaged over 1 nm. The cross-sections of Rattigan *et al.*[1] are higher than those of Meller and Moortgat[2] by approximately a factor of 2 at 230 nm. Although the two studies are nominally at comparable resolution, the Rattigan *et al.*[1] spectrum does not appear to contain all the features reported by Meller and Moortgat,[2] indicating possible errors.

References

[1] O. V. Rattigan, D. M. Rowley, O. Wild, R. L. Jones, and R. A. Cox, J. Chem. Soc. Faraday Trans. **90**, 1819 (1994).

[2] R. Meller and G. Moortgat, "Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere," Final Report to STEP-0004-C(EDB), 1992.

[3] L. K. Giddings and K. K. Innes, J. Mol. Spectrosc. **6**, 528 (1961).

[4] E. Klimeck and M. J. Berry, Chem. Phys. Lett. **20**, 141 (1973).

$COF_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$COF_2 + h\nu \rightarrow COF+F$	(1)	543	220
$\rightarrow CO+2F$	(2)	683	175
$\rightarrow CF_2+O(^3P)$	(3)	690	173

Preferred Values

Absorption cross-sections for COF_2 photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
186.0	5.5	205.1	0.74
187.8	4.8	207.3	0.52
189.6	4.2	209.4	0.40
191.4	3.7	211.6	0.28
193.2	3.1	213.9	0.20
195.1	2.6	216.2	0.12
197.0	2.1	218.6	0.081
199.0	1.6	221.0	0.049
201.0	1.3	223.5	0.035
203.0	0.95	226.0	0.024
		228.6	0.018

Quantum Yield for COF_2 Photolysis at 298 K

$\phi_1 = 1.0$ at $\lambda = 193$ nm.

Comments on Preferred Values

The preferred values of the absorption cross sections are those reported by Molina and Molina[1] over the wavelength range 184 to 199 nm and those reported in the recent study by Nolle *et al.*[2] at longer wavelengths. These results are in excellent agreement over the range 200–208 nm; from 208–225 nm the results of Molina and Molina[1] are 15–25% smaller than those of Nolle *et al.*[2] The spectrum shows considerable structure; the values listed are averages over 500 cm^{-1} intervals. The recommended quantum yield ($\phi_1 = 1.0$) is based on the results of the study of Nolle *et al.* at 193 nm, in which they monitored the decay of COF_2 and reported an apparent quantum yield of 0.47±0.03. Assuming that all the COF radicals produced in channel (1) regenerate COF_2 by the reaction 2 COF $\rightarrow COF_2$ + CO, a value of $\phi_1 = 0.94 \pm 0.06$ can be calculated.

References

[1] L. T. Molina and M. J. Molina, Results presented at the 182nd American Chemical Society National Meeting, New York, August 1982.

[2] A. Nolle, H. Heydtmann, R. Meller, W. Schneider, and G. K. Moortgat, Geophys. Res. Lett. 19, 281 (1992).

$CF_3CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_3CHO + h\nu \rightarrow CF_3+HCO$	(1)		
$\rightarrow CF_3CO + H$	(2)		
$\rightarrow CHF_3 + CO$	(3)		

Absorption cross-section data

Wavelength range/nm	References	Comments
230–360	Meller, Boglu, and Moortgat, 1993[1]	(a)

Comments

(a) Absolute absorption cross-sections were measured using a diode-array spectrometer over the temperature range 240–300 K. The UV spectrum of trifluoroacetaldehyde shows a broad band, centered at 305 nm and extending out to 355 nm. Values of σ were given at 5 nm intervals at 298 K.

Quantum Yield Data

There are no reported quantum yield data. The products of photolysis of CF_3CHO have been investigated by Dodd and Smith.[2] More recently, Richer *et al.*[3] have studied the photooxidation of CF_3CHO and observed CHF_3, CO, CO_2, and COF_2 as products. Photodissociation appears to occur predominantly via reaction (1). However, Richer *et al.*[3] observed substantial yields (14%) of CHF_3 in the 254 nm photolysis of CF_3CHO in air, indicating that channel (3) also occurs at that wavelength.

Preferred Values

Absorption cross sections at 298 K

λ/nm	10^{21} σ/cm^2	λ/nm	10^{21} σ/cm^2
235	0.74	300	29.8
240	1.29	305	29.0
245	2.17	310	27.9
250	3.44	315	25.0
255	5.25	320	21.4
260	7.63	325	17.7
265	10.6	330	13.6
270	13.8	335	9.98
275	17.6	340	6.17
280	21.3	345	3.86
285	24.8	350	2.31
290	27.6	355	0.59
295	29.1	360	0.19

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data reported by Meller *et al.*[1] In the absence of data, no recommendation is made for the quantum yields but by analogy with other aldehydes, which show a similar absorption spectrum, photodissociation at wavelengths >300 nm is expected to be predominantly by channel (1).

References

[1] R. Meller, D. Boglu, and G. K. Moortgat, "Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere," STEP-HALOCSIDE/AFEAS Workshop, Dublin, Eire, March 23–25, 1993, pp. 130–138.

[2] R. E. Dodd and J. Watson-Smith, J. Chem. Soc. 1465 (1957).

[3] H. Richer, J. R. Sodeau, and I. Barnes, "Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere," STEP-HALOCSIDE/AFEAS Workshop, Dublin, Eire, March 23–25, 1993, pp. 182–188.

$CF_3COF + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_3COF + h\nu \rightarrow CF_3 + FCO$ (1)		
$\rightarrow CF_3CO + F$ (2)		

Absorption cross-section data

Wavelength range/nm	References	Comments
200–340	Rattigan *et al.*, 1993[1]	(a)
210–265	Meller, Boglu, and Moortgat, 1993[2]	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(1)+\phi(2)=1.05\pm0.05$	254	Meller, Boglu, and Moortgat, 1993[2]	(c)

Comments

(a) Absolute absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 240–300 K. The UV spectrum of trifluoroacetyl fluoride shows a single band extending out to 315 nm, where there is significant temperature dependence. Values of σ were given at 5 nm intervals at 298 K and 240 K as well as temperature coefficients in the long wavelength tail at $\lambda > 270$ nm.

(b) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. Cross-sections were averaged over 1 nm, 2 nm, and 5 nm wavelength intervals.

(c) Average of 10 measurements of the overall loss of CF_3COF by photolysis in 1 atm air at 298 K, relative to the loss of $COCl_2$ for which $\phi = 1$.

Preferred Values

Absorption cross-sections at 293 and 238 K

λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$		$10^3 \times B/\mathrm{K}^{-1}$
	293 K	238 K	
200	9.35	9.46	−0.21
205	11.50	11.60	−0.16
210	12.88	13.10	−0.31
215	13.72	13.70	0.03
220	13.39	13.10	0.40
225	11.93	11.40	0.83
230	9.75	9.11	1.23
235	7.26	6.55	1.87
240	4.93	4.18	2.99
245	3.01	2.30	4.91
250	1.67	1.16	6.60
255	0.82	0.49	9.36
260	0.35	0.18	12.40
265	0.13	0.05	18.77
270	0.04	0.01	26.36
275	0.012	0.003	24.73
280	0.004	0.001	23.32
285	0.0016	0.0004	25.21
290	0.0008	0.00	
295	0.0003	0.00	

[a] Temperature dependence: $\log_e\{\sigma(T)/\sigma(293\ \mathrm{K})\} = B(T - 293)$.

Quantum Yields

$\phi(1) + \phi(2) = 1.0$ over the wavelength range 200–315 nm.

Comments on Preferred Values

The preferred values for the cross sections at 293 K are a simple average of the data reported by Rattigan *et al.*[1] and Meller *et al.*[2] The temperature dependence is based on the 238 K data of Rattigan *et al.*[1] The quantum yield of unity is based on the data of Meller *et al.*,[2] and is assumed to apply over the wavelength region 200–315 nm.

References

[1] O. V. Rattigan, O. Wild, R. L. Jones, and R. A. Cox, J. Photochem. Photobiol. A: Chem. **73**, 1 (1993).

[2] R. Meller, D. Boglu, and G. K. Moortgat, "Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere," STEP-HALOCSIDE/AFEAS Workshop, Dublin, Eire, March 23–25, 1993, pp. 130–138.

4.7. Chlorine Species

O + HOCl → HO + ClO

$\Delta H^\circ = -30\ \text{kJ}\cdot\text{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.3\pm0.2)\times10^{-13}$	298	Vogt and Schindler, 1992[1]	(a)
Reviews and Evaluations			
No recommendation		IUPAC, 1992[2]	(b)
$1.0\times10^{-11}\exp(-1300/T)$	200–300	NASA, 1994[3]	(c)

Comments

(a) Discharge fast flow system with mass spectrometric detection. Pseudo-first-order decay of [HOCl] in excess [O] measured.

(b) No recommendation because there were no experimental data.

(c) Based on the results of Vogt and Schindler[1] and an estimated A-factor.

Preferred Values

$k=1.3\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.0\times10^{-11}\exp(-1300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k=\pm0.7$ at 298 K.

$\Delta(E/R)=\pm1000$ K.

Comments on Preferred Values

The preferred values are based on the room temperature results of Vogt and Schindler.[1] This is the only experimental study of this reaction. The A factor was estimated based on O-atom reactions with similar compounds, and the E/R value fitted to the value of k(298 K).

References

[1] R. Vogt and R. N. Schindler, Geophys. Res. Lett. **19**, 1935 (1992).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

O + ClO → Cl + O_2

$\Delta H^\circ = -229.5\ \text{kJ}\cdot\text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k=3.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta\log k=\pm0.1$ at 298 K.

$\Delta(E/R)=\pm250$ K.

Comments on Preferred Values

The most recent studies all give values of k_{298} about 30% lower than the earlier work of Bemand *et al.*[1] and Clyne and Nip.[2] The two most recent studies[3,4] give a negative temperature dependence, in contrast to the earlier work which showed zero or positive temperature coefficients. The preferred value is independent of temperature and is obtained by averaging the 298 K values from Schwab *et al.*,[5] Nicovich *et al.*,[3] Ongstad and Birk,[4] Leu,[6] Margitan,[7] and Zahniser and Kaufman.[8] The uncertainty on E/R allows for a temperature dependence consistent with all studies. Leu and Yung[9] have recently shown that the yields of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ in the reaction are $<2.5\times10^{-2}$ and $(4.4\pm1.1)\times10^{-4}$, respectively. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[10]

References

[1] P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **69**, 1356 (1973).

[2] M. A. A. Clyne and W. S. Nip, J. Chem. Soc. Faraday Trans. 1, **72**, 221 (1976).

[3] J. M. Nicovich, P. H. Wine, and A. R. Ravishankara, J. Chem. Phys. **89**, 5670 (1988).

[4] A. P. Ongstad and J. W. Birks, J. Chem. Phys. **85**, 3359 (1986).

[5] J. J. Schwab, D. W. Toohey, W. H. Brune, and J. G. Anderson, J. Geophys. Res. **89**, 9581 (1984).

[6] M. T. Leu, J. Phys. Chem. **88**, 1394 (1984).

[7] J. J. Margitan, J. Phys. Chem. **88**, 3638 (1984).

[8] M. S. Zahniser and F. Kaufman, J. Chem. Phys. **66**, 3673 (1977).

[9] M. T. Leu and Y. Yung, Geophys. Res. Lett. **14**, 949 (1987).

[10] IUPAC, Supplement IV, 1992 (see references in Introduction).

O + OClO → O_2 + ClO

$\Delta H^\circ = -243.2\ \mathrm{kJ \cdot mol^{-1}}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.4 \times 10^{-12} \exp[-(960 \pm 120)/T]$	243–400	Gleason, Nesbitt, and Stief, 1994[1]	(a)
$(1.0 \pm 0.3) \times 10^{-13}$	298		
Reviews and Evaluations			
$2.5 \times 10^{-12} \exp(-950/T)$	240–400	IUPAC, 1992[2]	(b)
$2.4 \times 10^{-12} \exp(-960/T)$	240–400	NASA, 1994[3]	(c)

Comments

(a) Discharge flow system with resonance fluorescence detection of $O(^3P)$ atoms. Measurements were made over the temperature range 200–400 K. The data for the temperature range 243–400 K were fitted with the Arrhenius expression given in the table. Data at lower temperatures showed a negative temperature dependence.

(b) Based on the results of Gleason *et al.*[1] which were then unpublished and were slightly different from the final values published in Ref. 1.

(c) Based on the results of Gleason *et al.*[1]

Preferred Values

$k = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.4 \times 10^{-12} \exp(-960/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are based on the results of the discharge flow-resonance fluorescence study of Gleason *et al.*[1] Over the temperature range of the recommendation (240–300 K), the data were well fit by the Arrhenius expression given, but at lower temperatures down to 200 K there was an abrupt change to a negative temperature dependence. The extrapolated 298 K rate coefficient of Colussi[4] supports this value. It appears that the experiments of Bemand *et al.*[5] were complicated by secondary chemistry. The experiments of Colussi[4] and Colussi *et al.*[6] over an extended pressure range demonstrate the importance of the termolecular reaction (see separate data sheet on O + OClO + M). The preferred values are only slightly different from those in our previous evaluation, IUPAC, 1992,[2] which were based on then unpublished results of Gleason *et al.*[1]

References

[1] J. F. Gleason, F. L. Nesbitt, and L. J. Stief, J. Phys. Chem. **98**, 126 (1994).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] A. J. Colussi, J. Phys. Chem. **94**, 8922 (1990).
[5] P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **69**, 1356 (1973).
[6] A. J. Colussi, S. P. Sander, and R. R. Friedl, J. Phys. Chem. **96**, 4442 (1992).

O + OClO + M → ClO_3 + M

$\Delta H^\circ = -112.2\ \mathrm{kJ \cdot mol^{-1}}$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.8 \times 10^{-31} (T/298)^{-1} [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$ K.

Comments on Preferred Values

The preferred values are based on the data of Colussi[1] and Colussi *et al.*[2] and correspond to falloff curves with $F_c = 0.48$ at 298 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 3.1 \times 10^{-11}$ $(T/298)^1$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

See comment on k_0. The preferred values for k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] A. J. Colussi, J. Phys. Chem. **94**, 8922 (1990).

[2] A. J. Colussi, S. P. Sander, and R. R. Friedl, J. Phys. Chem. **96**, 4442 (1992).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O + Cl_2O \rightarrow ClO + ClO$

$\Delta H^\circ = -127.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.7 \times 10^{-11} \exp[-(510 \pm 30/T)]$	230–380	Stevens and Anderson, 1992[1]	(a)
$(4.7 \pm 0.2) \times 10^{-12}$	298		
Reviews and Evaluations			
$2.9 \times 10^{-11} \exp(-630/T)$	235–300	IUPAC, 1992[2]	(b)
$2.7 \times 10^{-11} \exp(-530/T)$	200–300	NASA, 1994[3]	(c)

Comments

(a) Discharge flow system. The pseudo-first-order decay of [O] in excess [Cl_2O] detected by resonance fluorescence.

(b) Based on the results of Miziolek and Molina[4] and of Wecker *et al.*[5]

(c) Based on the results of Stevens and Anderson[1] and Miziolek and Molina.[4]

Preferred Values

$k = 4.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.7 \times 10^{-11} \exp(-530/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–380 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred value at 298 K is based on the results of Stevens and Anderson[1] and Miziolek and Molina,[4] which are in good agreement. The significantly lower values of Wecker *et al.*[5] are not included, nor are earlier, higher results of Basco and Dogra[6] and Freeman and Phillips[7] due to data analysis difficulties in both studies.

References

[1] P. S. Stevens and J. G. Anderson, J. Phys. Chem. **96**, 1708 (1992).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] A. W. Miziolek and M. J. Molina, J. Phys. Chem. **82**, 1769 (1978).

[5] D. Wecker, R. Johanssen, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **86**, 532 (1982).

[6] N. Basco and S. K. Dogra, Proc. R. Soc. London, Ser. A **323**, 29 (1971).

[7] G. G. Freeman and L. F. Phillips, J. Phys. Chem. **72**, 3025 (1968).

$O + ClONO_2 \rightarrow ClO + NO_3$ (1)
$\rightarrow OClO + NO_2$ (2)
$\rightarrow O_2 + ClONO$ (3)

$\Delta H^\circ(1) = -96.8\ kJ\cdot mol^{-1}$
$\Delta H^\circ(2) = -143.3\ kJ\cdot mol^{-1}$
$\Delta H^\circ(3) = -216\ kJ\cdot mol^{-1}$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2 + k_3$)

$k = 2.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.0 \times 10^{-12} \exp(-800/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 213–295 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The results reported by Molina *et al.*,[1] Kurylo,[2] and Adler-Golden and Wiesenfeld[3] are in good agreement and have been used to derive the preferred Arrhenius expression. The value reported by Ravishankara *et al.*[4] is a factor of two higher, and this may possibly be attributed to secondary kinetic complications, the presence of NO_2 as a reactive impurity, or the formation of reactive photolytic products. None of the studies reported identification of the reaction products. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[5]

References

[1] L. T. Molina, J. E. Spencer, and M. J. Molina, Chem. Phys. Lett. **45**, 158 (1977).
[2] M. J. Kurylo, Chem. Phys. Lett. **45**, 158 (1977).
[3] S. M. Adler-Golden and J. R. Wiesenfeld, Chem. Phys. Lett. **82**, 281 (1981).
[4] A. R. Ravishankara, D. D. Davis, G. Smith, G. Tesi, and J. Spencer, Geophys. Res. Lett. **4**, 7 (1977).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O(^1D)$ + HCFCs → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.1×10^{-10} CHF_2Cl	298	Warren, Gierczak, and Ravishankara, 1991[1]	(a)
2.2×10^{-10} CH_3CF_2Cl			
2.6×10^{-10} CH_3CFCl_2			
1.2×10^{-10} CH_2ClCF_3			
8.6×10^{-11} $CHFClCF_3$			
2.0×10^{-10} $CHCl_2CF_3$			
Reviews and Evaluations			
9.5×10^{-11} CHF_2Cl	298	IUPAC, 1992[2]	(b)
1.9×10^{-10} $CHFCl_2$			
1.4×10^{-10} CH_3CF_2Cl			
1.5×10^{-10} CH_3CFCl_2			
1.5×10^{-10} CH_2ClCF_3			
1.6×10^{-10} CH_2ClCF_2Cl			
1.0×10^{-10} $CHFClCF_3$			
2.2×10^{-10} $CHCl_2CF_3$			
1.0×10^{-10} CHF_2Cl	200–300	NASA, 1994[3]	(c)
1.9×10^{-10} $CHFCl_2$			
2.2×10^{-10} CH_3CF_2Cl			
2.6×10^{-10} CH_3CFCl_2			
1.2×10^{-10} CH_2ClCF_3			
1.6×10^{-10} CH_2ClCF_2Cl			
8.6×10^{-11} $CHFClCF_3$			
2.0×10^{-10} $CHCl_2CF_3$			

Comments

(a) Laser flash photolysis of O_3 at 248 nm. Time-resolved production of $O(^3P)$ monitored by resonance fluorescence at 130 nm.

(b) CHF_2Cl and $CHFCl_2$: Based on the results of Davidson *et al.*[4] CH_3CF_2Cl, CH_2ClCF_3, CH_2ClCF_2Cl, and $CHCl_2CF_3$: Based on the results of Green and Wayne.[5] CH_3CFCl_2 and $CHFClCF_3$: Estimated by analogy.

(c) CHF_2Cl: Based on the results of Warren *et al.*[1] and Davidson *et al.*[4] $CHFCl_2$: Based on the results of Davidson *et al.*[4] CH_3CF_2Cl, CH_3CFCl_2, CH_2ClCF_3, $CHFClCF_3$, and $CHCl_2CF_3$: Based on the results of Warren *et al.*[1] CH_2ClCF_2Cl: Based on the results of Green and Wayne.[5]

Preferred Values

CHF_2Cl	$k=1.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 175–340 K.
$CHFCl_2$	$k=1.9\times10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 175–340 K.
CH_3CF_2Cl	$k=2.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CH_3CFCl_2	$k=2.6\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CH_2ClCF_3	$k=1.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CH_2ClCF_2Cl	$k=1.6\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$CHFClCF_3$	$k=8.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$CHCl_2CF_3$	$k=2.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K for CHF_2Cl.

$\Delta\log k=\pm0.2$ at 298 K for $CHFCl_2$, CH_3CF_2Cl, CH_3CFCl_2, CH_2ClCF_3, $CHFClCF_3$, and $CHCl_2CF_3$.

$\Delta\log k=\pm0.3$ at 298 K for CH_2ClCF_2Cl.

Comments on Preferred Values

The rate coefficients given are for the total disappearance of $O(^1D)$ atoms and include both physical quenching and chemical reaction. The rate coefficients for CHF_2Cl and $CHFCl_2$ have been determined to be temperature-independent over the range 175–340 K. Rate coefficients for the other HCFCs are also assumed to be temperature-independent by analogy with these two species and also considering that they have such high values at 298 K. Specific comments are as follows:

CHF_2Cl: Based on the results of Warren *et al.*[1] and Davidson *et al.*[4] Addison *et al.*[6] reported that the dominant channel leads to the formation of ClO (55±10%) and that the second most important channel leads to the elimination of HCl (40%). The latter process is accompanied by formation of CF_2 and $O(^3P)$. They also report an OH radical yield of 5%. Warren *et al.*[1] report an $O(^3P)$ yield of 28% which they interpret as the product of physical quenching.

$CHFCl_2$:	Based on the results of Davidson *et al.*[4]
CH_3CF_2Cl:	Based on the results of Warren *et al.*,[1] who also report 26% physical quenching.
CH_3CFCl_2:	Based on the results of Warren *et al.*,[1] who also report 31% physical quenching.
CH_2ClCF_3:	Based on the results of Warren *et al.*,[1] who also report 20% physical quenching.
CH_2ClCF_2Cl:	Based on the results of Green and Wayne.[5]
$CHFClCF_3$:	Based on the results of Warren *et al.*,[1] who also report 31% physical quenching.
$CHCl_2CF_3$:	Based on the results of Warren *et al.*,[1] who also report 21% physical quenching.

References

[1] R. Warren, T. Gierczak, and A. R. Ravishankara, Chem. Phys. Lett. **183**, 403 (1991).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] J. A. Davidson, H. I. Schiff, T. J. Brown, and C. J. Howard, J. Chem. Phys. **69**, 4277 (1978).

[5] R. G. Green and R. P. Wayne, J. Photochem. **6**, 371 (1976).

[6] M. C. Addison, R. J. Donovan, and J. Garraway, J. Chem. Soc. Faraday Discuss. **67**, 286, 1979.

$$O(^1D) + CF_2Cl_2 \rightarrow ClO + CF_2Cl \quad (1)$$

$$\rightarrow O(^3P) + CF_2Cl_2 \quad (2)$$

$$\rightarrow COF_2 + Cl_2 \quad (3)$$

$$\rightarrow COFCl + FCl \quad (4)$$

$\Delta H^\circ(1)=-123.1$ kJ·mol^{-1}
$\Delta H^\circ(2)=-189.7$ kJ·mol^{-1}
$\Delta H^\circ(3)=-580.3$ kJ·mol^{-1}
$\Delta H^\circ(4)=-423$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2 + k_3 + k_4$)

$k = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.15$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (k_2/k) = \pm 0.1$ K.

Comments on Preferred Values

The preferred values are based on the results of Force and Wiesenfeld[1] and Davidson *et al.*,[2] which are in excellent agreement. The weight of evidence from many O(^{1}D) rate studies suggests that the results of Fletcher and Husain[3] contain a systematic error. The results from the relative rate coefficient studies[4–6] were not considered in this evaluation. However, combining the values of k/k(O(^{1}D) + N$_2$O) reported in Refs. 4 and 5 with the IUPAC preferred value for k(O(^{1}D) + N$_2$O) yields values of k in good agreement with the preferred value. Both Donovan[7] and Force and Wiesenfeld[1] report that the quenching channel (2) is a significant removal pathway for O(^{1}D). Consequently, preferred values are given for both the overall rate constant, k, and for the branching ratio k_2/k. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[8]

References

[1] A. P. Force and J. R. Wiesenfeld, J. Phys. Chem. **85**, 782 (1981).
[2] J. A. Davidson, H. I. Schiff, T. J. Brown, and C. J. Howard, J. Chem. Phys. **69**, 4277 (1978).
[3] I. S. Fletcher and D. Husain, J. Phys. Chem. **80**, 1837 (1976).
[4] R. K. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **4**, 381 (1975).
[5] R. Atkinson, G. M. Breuer, J. N. Pitts, Jr., and H. L. Sandoval, J. Geophys. Res. **81**, 5765 (1976).
[6] R. G. Green and R. P. Wayne, J. Photochem. **6**, 371 (1977).
[7] R. J. Donovan, private communication (1980).
[8] IUPAC, Supplement IV, 1992 (see references in Introduction).

$\mathrm{O(^1D) + CFCl_3 \rightarrow ClO + CFCl_2}$ (1)
$\mathrm{\rightarrow O(^3P) + CFCl_3}$ (2)
$\mathrm{\rightarrow COFCl + Cl_2}$ (3)
$\mathrm{\rightarrow COCl_2 + FCl}$ (4)

$\Delta H^\circ(1) = -141.5$ kJ·mol^{-1}
$\Delta H^\circ(2) = -189.7$ kJ·mol^{-1}
$\Delta H^\circ(3) = -581$ kJ·mol^{-1}
$\Delta H^\circ(4) = -425$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2 + k_3 + k_4$)

$k = 2.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.16$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred values are based on the results of Force and Wiesenfeld[1] and Davidson *et al.*,[2] which are in excellent agreement. The weight of evidence from many O(^{1}D) rate studies suggests that the results of Fletcher and Husain[3] contain a systematic error.

The results from the relative rate coefficient studies[4,5] were not considered in this evaluation. However, combining the values of k/k(O(^{1}D) + N$_2$O) reported in Refs. 4 and 5 with the IUPAC preferred value for k(O(^{1}D) + N$_2$O) yields rate coefficients in good agreement with the preferred value. Both Donovan[6] and Force and Wiesenfeld[1] report that the quenching channel (2) is a significant removal pathway for O(^{1}D). Consequently, preferred values are given for both the overall rate constant, k, and for the branching ratio k_2/k. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[7]

References

[1] A. P. Force and J. R. Wiesenfeld, J. Phys. Chem. **85**, 782 (1981).
[2] J. A. Davidson, H. I. Schiff, T. J. Brown, and C. J. Howard, J. Chem. Phys. **69**, 4277 (1978).
[3] I. S. Fletcher and D. Husain, J. Phys. Chem. **80**, 1837 (1976).
[4] R. K. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **4**, 381 (1975).
[5] R. Atkinson, G. M. Breuer, J. N. Pitts, Jr., and H. L. Sandoval, J. Geophys. Res. **81**, 5765 (1976).
[6] R. J. Donovan, private communication (1980).
[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O(^1D) + CCl_4 \rightarrow ClO + CCl_3$ (1)
$\rightarrow O(^3P) + CCl_4$ (2)
$\rightarrow COCl_2 + Cl_2$ (3)

$\Delta H°(1) = -170.4$ kJ·mol^{-1}
$\Delta H°(2) = -189.7$ kJ·mol^{-1}
$\Delta H°(3) = -563.2$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2 + ik_3$)

$k = 3.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.14$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred values are based on the results of Force and Wiesenfeld[1] and Davidson *et al.*,[2] which are in excellent agreement. The weight of evidence from many $O(^1D)$ rate studies suggests that the data of Fletcher and Husain[3] contain a systematic error. The results from the relative rate coefficient study[4] was not considered in this evaluation. Combining the value of $k/k(O(^1D) + N_2O)$ reported in Ref. 4 with the IUPAC preferred value of $k(O(^1D) + N_2O)$ yields a value ~25% lower than the preferred value. The observation of a quenching channel in this reaction is consistent with the results from the $O(^1D)$ atom reactions with CF_2Cl_2 and $CFCl_3$. Consequently, preferred values are given for both the overall rate constant, k, and for the branching ratio k_2/k. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[5]

References

[1] A. P. Force and J. R. Wiesenfeld, J. Phys. Chem. **85**, 782 (1981).
[2] J. A. Davidson, H. I. Schiff, T. J. Brown, and C. J. Howard, J. Chem. Phys. **69**, 4277 (1978).
[3] I. S. Fletcher and D. Husain, J. Phys. Chem. **80**, 1837 (1976).
[4] R. K. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **4**, 381 (1975).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O(^1D) + COFCl \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k = 1.9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$.

Comments on Preferred Values

The preferred value is derived from the data of Fletcher and Husain[1] by use of a scaling factor of 0.5. The weight of evidence from many $O(^1D)$ rate studies suggests that $O(^1D)$ rates reported by Husain and co-workers[1] contain a systematic error, and that these results can be made consistent with other $O(^1D)$ recommended values in this evaluation by use of this scaling factor. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.[2]

References

[1] I. S. Fletcher and D. Husain, J. Photochem. **8**, 355 (1978).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O(^1D) + COCl_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=3.6\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.3$.

Comments on Preferred Values

The preferred value is derived from the data of Fletcher and Husain[1] by use of the scaling factor of 0.5. The weight of evidence from many O(^{1}D) atom rate studies suggests that O(^{1}D) rates reported by Husain and co-workers[1] contain a systematic error, and that these results can be made consistent with other O(^{1}D) recommended values in this evaluation by use of this scaling factor. Note that Jayanty *et al.*[2] present evidence, based on high yields of CO, that the reaction channel to produce ClO + ClCO is very important. The preferred value is identical to that in our previous evaluation, IUPAC, 1992.[3]

References

[1] I. S. Fletcher and D. Husain, J. Photochem. **8**, 355 (1978).

[2] R. K. M. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **5**, 217 (1976).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + H_2 \rightarrow HCl + H$

$\Delta H°=4.4$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=1.6\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=3.7\times10^{-11}\exp(-2300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k=\pm0.1$ at 298 K.

$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The preferred value is derived from a least-squares fit to data below 300 K reported by Watson *et al.*,[1] Lee *et al.*,[2] Miller and Gordon,[3] and Kita and Stedman.[4] The results of these studies are in excellent agreement below 300 K; at higher temperatures the data are in poorer agreement. After extrapolation, the results of Watson *et al.*,[1] Miller and Gordon,[3] and Kita and Stedman[4] agree with the results of Benson *et al.*[5] and Steiner and Rideal.[6] Note that the two most recent studies[3,4] have measured both the forward and reverse rates and have shown that the rate coefficient ratio agrees with equilibrium constant data. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[7]

References

[1] R. T. Watson, E. S. Machado, R. L. Schiff, S. Fischer, and D. D. Davis, Proceedings of the 4th CIAP Conference, DOT-OST-75, 1975.

[2] J. H. Lee, J. V. Michael, W. A. Payne, L. J. Stief, and D. A. Whytock, J. Chem. Soc. Faraday Trans. 1, **73**, 1530 (1977).

[3] J. C. Miller and R. J. Gordon, J. Chem. Phys. **75**, 5305 (1991).

[4] D. Kita and D. H. Stedman, J. Chem. Soc. Faraday Trans. 2, **78**, 1249 (1982).

[5] S. W. Benson, F. R. Cruickshank, and R. Shaw, Int. J. Chem. Kinet. **1**, 29 (1969).

[6] H. Steiner and E. K. Rideal, Proc. R. Soc. London, Ser. A **173**, 503 (1939).

[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + HO_2 \rightarrow HCl + O_2$ (1)
$\rightarrow ClO + HO$ (2)

$\Delta H°(1) = -228.2$ kJ·mol^{-1}
$\Delta H°(2) = 5.0$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.45 \pm 0.06) \times 10^{-11}$	243-368	Dobis and Benson, 1993[1]	(a)
Branching Ratios			
$k_2/k = 0.05 \pm 0.03$	243-368	Dobis and Benson, 1993[1]	(a)
Reviews and Evaluations			
$k_1 = 1.8 \times 10^{-11} \exp(170/T)$	250–420	IUPAC, 1992[2]	(b)
$k_2 = 4.1 \times 10^{-11} \exp(-450/T)$	250–420		
$k_1 = 1.8 \times 10^{-11} \exp(170/T)$	250–420	NASA, 1994[3]	(c)
$k_2 = 4.1 \times 10^{-11} \exp(-450/T)$	250–420		

Comments

(a) Ethyl radicals were formed by reaction of Cl atoms with C_2H_6 and allowed to react with O_2 in a very low pressure reactor (VLPR) flow system with mass spectrometric analysis of reactants and products.

(b) See Comments on Preferred Values.

(c) Based on the direct study of Lee and Howard[4] and supported by the room temperature results of Cattell and Cox.[5]

Preferred Values

$k_1 = 3.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 9.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 1.8 \times 10^{-11} \exp(170/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–420 K.
$k_2 = 4.1 \times 10^{-11} \exp(-450/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–420 K.

Reliability

$\Delta \log k_1 = \pm 0.2$ at 298 K.
$\Delta \log k_2 = \pm 0.3$ at 298 K.
$\Delta(E_1/R) = \Delta(E_2/R) = \pm 250$ K.

Comments on Preferred Values

The recommendation is unchanged from our previous evaluation, IUPAC, 1992.[2] The preferred values for k_1 and k_2 are based on results of the direct study by Lee and Howard.[4] These expressions were derived by the authors from data on the overall rate and the branching ratio. The total rate constant is temperature independent over the range 250–420 K with a value of 4.2×10^{-11} cm^3 molecule^{-1} s^{-1}. The room temperature results of Cattell and Cox[5] are in good agreement with this recommendation. Based on the combined results of these two studies, neither channel shows any pressure dependence between 1 mbar and 1 bar showing that stabilization of the HOOCl* intermediate does not occur, the two bimolecular channels making up the entire reaction pathway. The recent study of Dobis and Benson[1] reports a total rate constant in good agreement with this recommendation but a significantly lower value of the branching ratio k_2/k. Results of earlier indirect studies[6–9] were not used.

References

[1] O. Dobis and S. W. Benson, J. Am. Chem. Soc. **115**, 8798 (1993).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] Y.-P. Lee and C. J. Howard, J. Chem. Phys. **77**, 756 (1982).
[5] F. C. Cattell and R. A. Cox, J. Chem. Soc. Faraday Trans. 2, **82**, 1413 (1986).
[6] M. T. Leu and W. B. DeMore, Chem. Phys. Lett. **41**, 121 (1976).
[7] G. Poulet, G. Le Bras, and J. Combourieu, J. Chem. Phys. **69**, 767 (1978).
[8] J. P. Burrows, D. I. Cliff, G. W. Harris, B. A. Thrush, and J. P. T. Wilkinson, Proc. R. Soc. London, Ser. A **368**, 436 (1979).
[9] R. A. Cox, Int. J. Chem. Kinet. **12**, 649 (1980).

$Cl + H_2O_2 \rightarrow HCl + HO_2$

$\Delta H° = -62.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=4.1\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=1.1\times10^{-11}\exp(-980/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 265–424 K.

Reliability
$\Delta\log k=\pm0.2$ at 298 K.
$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The room temperature rate coefficients reported in Refs. 1–5 range from $(3.6\text{–}6.2)\times10^{-13}$ cm^3 molecule^{-1} s^{-1}. The studies of Michael *et al.*,[3] Poulet *et al.*,[4] and Keyser[5] are considered to be the most reliable. The recommended Arrhenius expression is that reported by Keyser.[5] The data of Michael *et al.*[3] below 300 K are in good agreement; however, the *A*-factor reported is considerably lower than that expected from theoretical considerations and may possibly be attributed to decomposition of H_2O_2 above 300 K. More data are required before the Arrhenius parameters can be considered to be well established. Heneghan and Benson[6] using mass spectrometry confirmed that this reaction proceeds only by the H-atom abstraction mechanism. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[7]

References

[1] R. T. Watson, G. Machado, S. Fischer, and D. D. Davis, J. Chem. Phys. **65**, 2126 (1976).
[2] M. T. Leu and W. B. DeMore, Chem. Phys. Lett. **41**, 121 (1976).
[3] J. V. Michael, D. A. Whytock, J. H. Lee, W. A. Payne, and L. J. Stief, J. Chem. Phys. **67**, 3533 (1977).
[4] G. Poulet, G. Le Bras, and J. Combourieu, J. Chem. Phys. **69**, 767 (1978).
[5] L. F. Keyser, J. Phys. Chem. **84**, 11 (1980).
[6] S. P. Heneghan and S. W. Benson, Int. J. Chem. Kinet. **15**, 1311 (1983).
[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + O_2 + M \rightarrow ClOO + M$

$\Delta H^\circ=-23.8$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0=1.4\times10^{-33}(T/300)^{-3.9}[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 160–300 K.
$k_0=1.6\times10^{-33}(T/300)^{-2.9}[O_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 160–300 K.

Reliability
$\Delta\log k_0=\pm0.2$ at 200 K.
$\Delta n=\pm1$.

Comments on Preferred Values

The two recent determinations[1,2] are in good agreement and are also consistent with the older data of Ref. 3, if one takes into account the strong temperature dependence of k_0. The most extensive measurements of Ref. 2 are the basis for the preferred values. No falloff expressions are reported here, because deviations from third order behavior become apparent only at pressures higher than 10 bar and because the falloff formalism does not apply to the radical-complex mechanism operating in this case. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] J. M. Nicovich, K. D. Kreutter, C. J. Shackelford, and P. H. Wine, Chem. Phys. Lett. **179**, 367 (1991).
[2] S. Baer, H. Hippler, R. Rahn, M. Siefke, N. Seitzinger, and J. Troe, J. Chem. Phys. **95**, 6463 (1991).
[3] J. E. Nicholas and R. G. W. Norrish, Proc. R. Soc. London, Ser. A **307**, 391 (1968).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$ClOO + M \rightarrow Cl + O_2 + M$

$\Delta H^\circ=23.8$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0=6.2\times10^{-13}$ [N_2] s^{-1} at 298 K.
$k_0=2.8\times10^{-10}\exp(-1820/T)$ [N_2] s^{-1} over the temperature range 200–300 K.

Reliability
$\Delta\log k_0=\pm0.3$ at 298 K.
$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The preferred values are based on the extensive data of Ref. 1. No deviations from third-order behavior were observed at pressures below 1 bar. The reaction probably does not proceed via an energy transfer mechanism (see comments on the reverse reaction $Cl + O_2 + M \rightarrow ClOO + M$), but rather by a radical complex mechanism. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[2]

References

[1] S. Baer, H. Hippler, R. Rahn, M. Siefke, N. Seitzinger, and J. Troe, J. Chem. Phys. **95**, 6463 (1991).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + CO + M \rightarrow ClCO + M$

$\Delta H° = -32.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.1\pm3.0)\times10^{-34}$ [Ar]	300	Clark, Clyne, and Stedman, 1966[1]	(a)
$1.05\times10^{-34}\exp[(810\pm70)/T]$ [N_2]	185–260	Nicovich, Kreutter, and Wine, 1990[2]	(b)
Reviews and Evaluations			
$1.3\times10^{-33}(T/300)^{-3.8}$ [air]	200–300	NASA, 1994[3]	(c)

Comments

(a) Discharge-flow system study of Cl_2-He mixtures. Cl atom concentrations were measured by titration with nitrosyl chloride using the red chlorine afterglow spectrum. The total pressure was 2–4 Torr. From experiments performed also at 195 K, an activation energy of about 8.4 kJ mol^{-1} was obtained.

(b) Laser flash photolysis of Cl_2-CO-M ($M=N_2$, CO, Ar, CO_2) mixtures at 355 nm. Detection of $Cl(^2P_{3/2})$ was by time-resolved resonance fluorescence spectroscopy. The total pressure was 14–200 Torr. By second- and third-law analysis of the temperature dependence of the equilibrium constant the value of $\Delta H^\circ_{298}=-32.2\pm2.5$ kJ mol^{-1} was derived. The relative collision efficiencies were $\beta_c(CO_2) : \beta_c(CO/N_2) : \beta_c(Ar) = 3.2 : 1.0 : 0.8$.

(c) Value adopted from Ref. 2.

Preferred Values

$k_0=1.3\times10^{-33}(T/300)^{-3.8}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 185–300 K.

Reliability
$\Delta\log k_0=\pm0.3$ at 298 K.
$\Delta n=\pm1$.

Comments on Preferred Values

The recommended rate coefficients are based on the measurements of Ref. 2. At room temperature the preferred value is a factor of two greater than that determined by Clark *et al.*[1]

References

[1] T. C. Clark, M. A. A. Clyne, and D. H. Stedman, Trans. Faraday Soc. **62**, 3354 (1966).
[2] J. M. Nicovich, K. D. Kreutter, and P. H. Wine, J. Chem. Phys. **92**, 3539 (1990).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$ClCO + M \rightarrow Cl + CO + M$

$\Delta H° = 32.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
4.1×10^{-10} exp[$-(2960 \pm 160)/T$] [N_2]	185–260	Nicovich, Kreutter, and Wine, 1990[1]	(a)

Comments

(a) Laser flash photolysis of Cl_2-CO-M ($M = N_2$, CO, Ar, CO_2) mixtures at 355 nm. Detection of $Cl(^2P_{3/2})$ was by time-resolved resonance fluorescence spectrum. The total pressure was 14–200 Torr. By second- and third-law analysis of the temperature dependence of the equilibrium constant, the value of $\Delta H°_{298} = 32.2 \pm 2.5$ kJ mol^{-1} was derived. The relative collision efficiencies were $\beta_c(CO_2)$: $\beta_c(CO/N_2)$: $\beta_c(Ar) = 3.2 : 1.0 : 0.8$.

Preferred Values

$k_0 = 2.0 \times 10^{-14}$ [N_2] s^{-1} at 298 K.

$k_0 = 4.1 \times 10^{-10}$ exp($-2960/T$) [N_2] s^{-1} over the temperature range 185–300 K.

Reliability

$\Delta \log k_0 = \pm 0.4$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred rate coefficients are based on the reported study of Nicovich *et al.*[1]

References

[1] J. M. Nicovich, K. D. Kreutter, and P. H. Wine, J. Chem. Phys. **92**, 3539 (1990).

$Cl + O_3 \rightarrow ClO + O_2$

$\Delta H° = -162.4$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.9 \times 10^{-11}$ exp($-260/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 205–298 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred Arrhenius expression is derived from a fit to the data within the temperature range 205–298 K reported from the studies of Watson *et al.*,[1] Zahniser *et al.*,[2] Kurylo and Braun,[3] and Clyne and Nip.[4] In this temperature range the rate constants at any particular temperature agree to within 30–40%. Results of the study by Nicovich *et al.*[5] show non-Arrhenius behavior over the temperature range 189–385 K. These results are in very good agreement with the present recommendation above about ~250 K; at lower temperatures they are higher than the recommendation although still within its stated uncertainty down to about 220 K.

Vanderzanden and Birks[6] have interpreted their observation of oxygen atoms in this system as evidence for some production (0.1–0.5%) of $O_2(^1\Sigma_g)$ in this reaction. The possible production of singlet molecular oxygen in this reaction has also been discussed by DeMore[7] in connection with the Cl_2 photosensitized decomposition of ozone. However, Choo and Leu[8] were unable to detect $O_2(^1\Sigma)$ or $O_2(^1\Delta)$ in the Cl + O_3 system and set upper limits to the branching ratios for their production of 5×10^{-4} and 2.5×10^{-2}, respectively. They suggested two possible mechanisms for the observed production of oxygen atoms, involving reactions of vibrationally excited ClO radicals with O_3 or with Cl atoms, respectively. Burkholder *et al.*[9] in a study of infrared line intensities of the ClO radical present evidence in support of the second mechanism. In their experiments with excess Cl atoms, the vibrationally excited ClO radicals produced in the Cl + O_3 reaction can react with Cl atoms to give Cl_2 and oxygen atoms which can then remove additional ClO radicals. These authors point out the possibility for systematic error from assuming a 1:1 stoichiometry for [ClO] : $[O_3]_0$ when using the Cl + O_3 reaction as a quantitative source of ClO radicals for kinetic and spectroscopic studies. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[10]

References

[1] R. T. Watson, G. Machado, S. Fischer, and D. D. Davis, J. Chem. Phys. **65**, 2126 (1976).
[2] M. S. Zahniser, F. Kaufman, and J. G. Anderson, Chem. Phys. Lett. **37**, 226 (1976).
[3] M. J. Kurylo and W. Braun, Chem. Phys. Lett. **37**, 232 (1976).
[4] M. A. A. Clyne and W. S. Nip, J. Chem. Soc. Faraday Trans. 2, **72**, 838 (1976).
[5] J. M. Nicovich, K. D. Kreutter, and P. H. Wine, Int. J. Chem. Kinet. **22**, 399 (1990).
[6] J. W. Vanderzanden and J. W. Birks, Chem. Phys. Lett. **88**, 109 (1982).
[7] W. B. DeMore, presented at 182nd National Meeting, American Chemical Society, New York, August 1981.
[8] K. Y. Choo and M.-T. Leu, J. Phys. Chem. **89**, 4832 (1985).
[9] J. B. Burkholder, P. D. Hammer, and C. J. Howard, J. Geophys. Res. **94**, 2225 (1989).
[10] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + HONO_2 \rightarrow HCl + NO_3$

$\Delta H° = -4.8$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k < 2.0 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit to the rate coefficient is based on the work of Wine *et al.*[1] The data in Refs. 1 and 2 show that the earlier data of Kurylo *et al.*[3] were well above the true value for the rate coefficient of this reaction. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] P. H. Wine, J. R. Wells, and J. M. Nicovich, J. Phys. Chem. **92**, 2223 (1988).
[2] H. Zagogianni, A. Mellouki, and G. Poulet, C. R. Acad. Sci., Series 2, 573 (1987).
[3] M. J. Kurylo, J. L. Murphy, and G. L. Knable, Chem. Phys. Lett. **94**, 281 (1983).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + NO_3 \rightarrow ClO + NO_2$

$\Delta H° = -60.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.26 \pm 0.17) \times 10^{-11}$	298	Becker *et al.*, 1991[1]	(a)
Reviews and Evaluations			
2.6×10^{-11}	200–300	IUPAC, 1992[2]	(b)
2.4×10^{-11}	200–300	NASA, 1994[3]	(c)

Comments

(a) Discharge flow-mass spectrometric technique. Two sets of experiments were performed, with monitoring of either the decay of Cl in excess NO_3 or the decay of NO_3 in excess Cl.
(b) Based on the results of Mellouki *et al.*[4]
(c) Based on the results of Becker *et al.*[1] and Mellouki *et al.*[4]

Preferred Values

$k = 2.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred value at room temperature is based on the studies of Becker *et al.*[1] and Mellouki *et al.*[4] The results of these direct absolute rate studies are preferred over those of earlier relative rate studies,[5–7] in which NO_3 was monitored in the photolysis of Cl_2-$ClONO_2$-N_2 mixtures. The agreement among these earlier studies[5–7] is not good and probably arises from complications in the chemistry of the systems used. This radical-radical reaction is expected to have negligible temperature dependence, which is consistent with the results of Cox *et al.*[7]

References

[1] E. Becker, U. Wille, A. D. Parr, and R. P. Wayne, Ber. Bunsenges. Phys. Chem. **95**, 1173 (1991).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] A. Mellouki, G. Le Bras, and G. Poulet, J. Phys. Chem. **91**, 5760 (1987).

[5] R. A. Cox, R. A. Barton, E. Ljungstrom, and D. W. Stocker, Chem. Phys. Lett. **108**, 228 (1984).

[6] J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, J. Phys. Chem. **89**, 4848 (1985).

[7] R. A. Cox, M. Fowles, D. Moulton, and R. P. Wayne, J. Phys. Chem. **91**, 3361 (1987).

$Cl + OClO \rightarrow ClO + ClO$

$\Delta H^\circ = -13.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 5.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.4 \times 10^{-11} \exp(160/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 298–450 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The data of Toohey[1] agree well with the previous work of Bemand *et al.*[2] at 298 K, but show a small negative temperature dependence over a similar range to that over which Bemand *et al.*[2] saw little change in k. The preferred value is the average of the 298 K values from these two studies[1,2] and the temperature dependence of Toohey[1] is accepted but with error limits covering the possibility that k is independent of temperature. Earlier work in Refs. 3 and 4 is rejected following the recommendation of Bemand *et al.*[2] The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[5]

References

[1] D. W. Toohey, "Kinetic and Mechanistic Studies of Reactions of Bromine and Chlorine Species Important in the Earth's Stratosphere," Ph.D. Thesis, Harvard University, Cambridge, MA (1988).

[2] P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **69**, 1356 (1973).

[3] N. Basco and S. K. Dogra, Proc. R. Soc. London, Ser. A **323**, 417 (1971).

[4] V. I. Gritsan, V. N. Panfilov, and I. L. Sukhanov, Reaction Kinetics and Catalysis Letters **2**, 265 (1975).

[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + Cl_2O \rightarrow Cl_2 + ClO$

$\Delta H^\circ = -101.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.0 \times 10^{-11} \exp[(127 \pm 30)/T]$	233-373	Stevens and Anderson, 1992[1]	(a)
$(9.1 \pm 0.4) \times 10^{-11}$	298		
Reviews and Evaluations			
9.8×10^{-11}	200–300	IUPAC, 1992[2]	(b)
$6.2 \times 10^{-11} \exp(130/T)$	230–370	NASA, 1994[3]	(c)

Comments

(a) Discharge flow system. The pseudo-first-order decay of [Cl] in excess [Cl_2O] was detected by resonance fluorescence.
(b) Based on the results of Ray *et al.*[4]
(c) Based on the results of Stevens and Anderson[1] and Ray *et al.*[4]

Preferred Values

$k=9.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=6.2\times10^{-11}$ exp(130/T) over the temperature range 233–373 K.

Reliability
$\Delta\log k=\pm0.1$ at 298 K.
$\Delta(E/R)=\pm130$ K.

Comments on Preferred Values

The preferred room temperature value is the mean of the value reported by Stevens and Anderson[1] and the values obtained by Ray *et al.*[4] using two completely independent techniques. This value has been confirmed by the relative rate study of Burrows and Cox.[5] The much lower value reported earlier by Basco and Dogra[6] has been rejected. The recommended temperature dependence is from Stevens and Anderson.[1] The agreement between the low-pressure studies and the high-pressure study implies that there is no pressure dependence over the pressure range 1 mbar–1 bar.

References

[1] P. S. Stevens and J. G. Anderson, J. Phys. Chem. **96**, 1708 (1992).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] G. W. Ray, L. F. Keyser, and R. T. Watson, J. Phys. Chem. **84**, 1674 (1980).
[5] J. P. Burrows and R. A. Cox, J. Chem. Soc. Faraday Trans. 1, **77**, 2465 (1981).
[6] N. Basco and S. K. Dogra, Proc. R. Soc. London, Ser. A **323**, 401 (1971).

$Cl + Cl_2O_2 \rightarrow Cl_2 + ClOO$

$\Delta H^\circ=-151.4$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=1.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 230–298 K.

Reliability
$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The preferred value is based on results of the discharge flow-mass spectrometric study of Friedl[1] and the relative rate study of Cox and Hayman.[2] The Arrhenius parameters have not been determined experimentally; however, the agreement of the room temperature value and that at 233 K along with the high value of k precludes a significant temperature dependence. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] R. R. Friedl, unpublished data (1991).
[2] R. A. Cox and G. D. Hayman, Nature **332**, 796 (1988).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$

$\Delta H^\circ=-70.5$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=1.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=6.8\times10^{-12}$ exp(160/T) cm^3 molecule^{-1} s^{-1} over the temperature range 219–298 K.

Reliability
$\Delta\log k=\pm0.12$ at 298 K.
$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The preferred value averages the results of Margitan[1] and Kurylo *et al.*,[2] which are in good agreement. These results show that the rate coefficient for this reaction is two orders of magnitude greater than was indicated by the previous study of Kurylo and Manning.[3] It now seems likely that the reaction actually being observed by Kurylo and Manning[3] was the slower reaction $O(^3P) + ClONO_2$. Margitan[1] has shown that the reaction proceeds by Cl atom abstraction rather than by O-atom abstraction. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] J. J. Margitan, J. Phys. Chem. **87**, 674 (1983).

[2] M. J. Kurylo, G. L. Knable, and J. L. Murphy, Chem. Phys. Lett. **95**, 9 (1983).

[3] M. J. Kurylo and R. G. Manning, Chem. Phys. Lett. **48**, 279 (1977).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + CH_4 \rightarrow HCl + CH_3$

$\Delta H^\circ = 7.2$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.6 \times 10^{-12} \exp(-1350/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

The preferred value at 298 K is obtained by taking the mean from the most reliable absolute (Watson *et al.*,[1] Manning and Kurylo,[2] Whytock *et al.*,[3] Michael and Lee,[4] Lin *et al.*,[5] Zahniser *et al.*,[6] Keyser,[7] and Ravishankara and Wine[8]) and the most reliable relative (Pritchard *et al.*,[9,10] Knox,[11] Knox and Nelson,[12] and Lin *et al.*[5]) rate coefficient studies. The room temperature absolute rate coefficients of Dobis and Benson[13] and Sawerysyn *et al.*[14] are in good agreement with the preferred value, which is identical to our previous evaluation, IUPAC, 1992.[15]

The preferred Arrhenius expression is derived to best fit all the reliable experimental data between 200 and 300 K. Data obtained above 300 K are not considered due to the nonlinear Arrhenius behavior observed in the absolute rate coefficient studies.[3,5,7,8] The average values of k at 230 K are: 3.19×10^{-14} cm^3 molecule^{-1} s^{-1} (flash photolysis);[1,2,3,8] 2.67×10^{-14} cm^3 molecule^{-1} s^{-1} (discharge flow);[6,7] and 2.27×10^{-14} cm^3 molecule^{-1} s^{-1} (competitive chlorination).[5,9–12] These differences increase at lower temperatures. Ravishankara and Wine[8] have suggested that the results obtained using the discharge flow and competitive chlorination techniques may be in error at the lower temperatures ($T < 240$ K) due to a nonequilibration of the $^2P_{1/2}$ and $^2P_{3/2}$ states of atomic chlorine. The chemical composition in each of the flash photolysis studies contained an efficient spin equilibrator, whereas this was not the case in the discharge flow studies. However, the reactor walls in the discharge flow studies could have been expected to have acted as an efficient spin equilibrator. Consequently, until the hypothesis of Ravishankara and Wine[8] is proven, it is assumed that the discharge flow and competitive chlorination results are reliable. The Arrhenius expression is derived to yield the preferred values of k at 298 K (1.04×10^{-13} cm^3 molecule^{-1} s^{-1}) and at 230 K (2.71×10^{-14} cm^3 molecule^{-1} s^{-1}, this is a simple mean of the three average values obtained from each of the three techniques). The preferred expression of $9.6 \times 10^{-12} \exp(-1350/T)$ cm^3 molecule^{-1} s^{-1} yields rate coefficients similar to those obtained in the discharge flow-resonance fluorescence studies. If only flash photolysisresonance fluorescence results are used, then an alternate expression of $6.4 \times 10^{-12} \times \exp(-1220/T)$ cm^3 molecule^{-1} s^{-1} is obtained (k at 298 K$=1.07 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and k at 230 K$=3.19 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}). It should be noted that the rate coefficient ratios $k(Cl + O_3)/k(Cl + CH_4)$ determined by DeMore[16] at 197 K and 217 K are in reasonable agreement with the present evaluations for these reactions (see the data sheet on the $Cl + O_3$ reaction).

References

[1] R. T. Watson, G. Machado, S. Fischer, and D. D. Davis, J. Chem. Phys. **65**, 2126 (1976).

[2] R. G. Manning and M. J. Kurylo, J. Phys. Chem. **81**, 291 (1977).

[3] D. A. Whytock, J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, J. Chem. Phys. **66**, 2690 (1977).

[4] J. V. Michael and J. H. Lee, Chem. Phys. Lett. **51**, 303 (1977).

[5] C. L. Lin, M. T. Leu, and W. B. DeMore, J. Phys. Chem. **82**, 172 (1978).

[6] M. S. Zahniser, B. M. Berquist, and F. Kaufman, Int. J. Chem. Kinet. **10**, 15 (1978).

[7] L. F. Keyser, J. Chem. Phys. **69**, 214 (1978).

[8] A. R. Ravishankara and P. H. Wine, J. Chem. Phys. **72**, 25 (1980).

[9] H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, J. Am. Chem. Soc. **76**, 1201 (1954).

[10] H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, J. Am. Chem. Soc. **77**, 2629 (1955).

[11] J. H. Knox, Chem. Indust. 1631 (1955); modified by authors of reference 5.

[12] J. H. Knox and R. L. Nelson, Trans. Faraday Soc. **55**, 937 (1959).

[13] O. Dobis and S. W. Benson, Int. J. Chem. Kinet. **19**, 691 (1987).

[14] J.-P. Sawerysyn, C. Lafage, B. Meriaux, and A. Tighezza, J. Chim. Phys. **84**, 1187 (1987).

[15] IUPAC, Supplement IV, 1992 (see references in Introduction).

[16] W. B. DeMore, J. Geophys. Res. **96**, 4995 (1991).

$Cl + C_2H_2 + M \rightarrow C_2H_2Cl + M$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
5.4×10^{-30} $(T/300)^{-2.09}$ [air]	252–370	Kaiser, 1992[1]	(a)
Reviews and Evaluations			
6.0×10^{-30} $(T/300)^{-3.5}$ [N_2]	200–300	IUPAC, 1992[2]	(b)
5.4×10^{-30} $(T/300)^{-2.1}$ [air]	200–300	NASA, 1994[3]	(c)

Comments

(a) Mixtures of Cl_2, C_2H_2, and C_2H_6 and the diluent gases air, N_2, and SF_6 were irradiated with an UV fluorescence lamp. After irradiation, C_2H_2 and C_2H_6 concentrations were monitored by GC. The measurements were carried out at 25-1300 Torr total pressure. Rate measurements were relative to the rate coefficient for the reaction $Cl + C_2H_6 \rightarrow C_2H_5 + HCl$, for which an average rate coefficient from Refs. 4-6 of $8.68 \times10^{-11} \exp(-225/T)$ cm^3 molecule^{-1} s^{-1} was adopted. Extrapolations were performed with $F_c=0.6$.

(b) The preferred values are averages of k_0 from Refs. 7 and 8, assuming equal rates for M=Ar and N_2. The temperature dependence is from Ref. 7.

(c) Based on measurements from Ref. 1.

Preferred Values

$k_0=5.7\times10^{-30}$ $(T/300)^{-3}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_0=\pm0.3$ at 298 K.

$\Delta n=\pm1$.

Comments on Preferred Values

Our previous preferred values[2] have been slightly modified to accommodate the recent determination by Kaiser.[1]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
2.13×10^{-10} $(T/300)^{-1.05}$	252–370	Kaiser, 1992[1]	(a)
Reviews and Evaluations			
2.3×10^{-10}	200–300	IUPAC, 1992[2]	(b)
2.1×10^{-10} $(T/300)^{-1.0}$	200–300	NASA, 1994[3]	(c)

Comments

(a) See comment (a) for k_0.

(b) Based on the measurements from Ref. 8.

(c) See comment (c) for k_0.

Preferred Values

$k_\infty=2.3\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta\log k_\infty=\pm0.3$ at 298 K.

$\Delta n=\pm1$.

Comments on Preferred Values

The preferred value is identical to our previous evaluation, IUPAC, 1992.[2] The temperature dependence of k_∞ given by Kaiser[1] is sensitive to the F_c value employed, which was constant ($F_c=0.6$). The values of Refs. 1 and 2 are in very good agreement at room temperature.

References

[1] E. W. Kaiser, Int. J. Chem. Kinet. **24**, 179 (1992).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] O. Dobis and S. W. Benson, J. Am. Chem. Soc. **112**, 1023 (1990).
[5] R. G. Manning and M. J. Kurylo, J. Phys. Chem. **81**, 291 (1977).
[6] R. S. Lewis, S. P. Sander, S. Wagner, and R. T. Watson, J. Phys. Chem. **84**, 2009 (1980).
[7] J. Brunning and L. J. Stief, J. Chem. Phys. **83**, 1005 (1985).
[8] T. J. Wallington, J. M. Andino, I. M. Lorkovic, E. W. Kaiser, and G. Marston, J. Phys. Chem. **94**, 3644 (1990).

$Cl + C_2H_4 + M \rightarrow C_2H_4Cl + M$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.6 \times 10^{-29} (T/300)^{-3.5}$ [air] cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

Ref. 1 is the only measurement in the falloff range which allows for an extrapolation to k_0. The preferred values are based on Ref. 1 and an estimated temperature dependence such as observed for $Cl + C_2H_2 + M \rightarrow ClC_2H_2 + M$ (see this evaluation).

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The falloff extrapolation of the data from Ref. 1 with $F_c = 0.6$ is consistent with results in the intermediate falloff range. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[2]

References

[1] T. J. Wallington, J. M. Andino, I. M. Lorkovic, E. W. Kaiser, and G. Marston, J. Phys. Chem. **94**, 3644 (1990).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + C_2H_6 \rightarrow HCl + C_2H_5$

$\Delta H^\circ = -8.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.20 \times 10^{-11} \exp[-(86 \pm 10)/T]$	203–343	Dobis and Benson, 1991[1]	(a)
$(6.10 \pm 0.11) \times 10^{-11}$	298		
$(7.05 \pm 1.4) \times 10^{-11}$	298	Kaiser *et al.*, 1992[2]	(b)
$(5.9 \pm 0.6) \times 10^{-11}$	297±2	Stickel *et al.*, 1992[3]	(c)
Reviews and Evaluations			
$8.2 \times 10^{-11} \exp(-100/T)$	220–600	IUPAC, 1992[4]	(d)
$7.7 \times 10^{-11} \exp(-90/T)$	220–350	NASA, 1994[5]	(e)

Comments

- (a) Very low pressure reactor study. Cl atoms were generated by microwave discharge of Cl_2-He mixtures, with MS analysis of reactants and products.
- (b) Cl atoms were generated by the laser photolysis of Cl_2 at 351 nm, with detection of the HCl product by time-resolved IR spectroscopy. The rate coefficient was obtained from the measured formation rate of HCl.
- (c) Cl atoms were generated by the laser photolysis of $C(O)Cl_2$ at 266 nm, with detection of the HCl product by time-resolved tunable diode laser absorption spectroscopy. The rate coefficient was obtained from the measured formation rate of HCl.
- (d) The 298 K rate coefficient was the average of the room temperature rate coefficients of Davis *et al.*,[6] Manning and Kurylo,[7] Ray *et al.*,[8] Lewis *et al.*,[9] and Dobis and Benson.[10] The temperature dependence was the average of those from the studies of Manning and Kurylo[7] and Lewis *et al.*[9]
- (e) The 298 K rate coefficient was the mean of the absolute rate coefficients of Davis *et al.*[6] Manning and Kurylo,[7] Ray *et al.*,[8] and Lewis *et al.*,[9] with the temperature dependence being that which best fit the data of Manning and Kurylo[7] and Lewis *et al.*[9]

Preferred Values

$k=5.9\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k=8.1\times10^{-11}\exp(-95/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 220–600 K.

Reliability

$\Delta\log k=\pm0.06$ at 298 K.
$\Delta(E/R)=\pm100$ K.

Comments on Preferred Values

The 298 K rate coefficient is the average of the room temperature rate coefficients of Davis *et al.*[6] (reduced by 10% as discussed previously[4]), Manning and Kurylo,[7] Ray *et al.*,[8] Lewis *et al.*,[9] Dobis and Benson,[1,10] and Stickel *et al.*,[3] all of which are in excellent agreement. The temperature dependence is the average of those from the temperature-dependent studies of Manning and Kurylo,[7] Lewis *et al.*,[9] and Dobis and Benson.[1] The room temperature rate coefficients of Poulet *et al.*[11] and Kaiser *et al.*[2] are in agreement with the preferred 298 K rate coefficient.

References

[1] O. Dobis and S. W. Benson, J. Am. Chem. Soc. **113**, 6377 (1991).
[2] E. W. Kaiser, L. Rimai, E. Schwab, and E. C. Lim, J. Phys. Chem. **96**, 303 (1992).
[3] R. E. Stickel, J. M. Nicovich, S. Wang, Z. Zhao, and P. H. Wine, J. Phys. Chem. **96**, 9875 (1992).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).
[5] NASA Evaluation No. 11, 1994 (see references in Introduction).
[6] D. D. Davis, W. Braun, and A. M. Bass, Int. J. Chem. Kinet. **2**, 101 (1970).
[7] R. G. Manning and M. J. Kurylo, J. Phys. Chem. **81**, 291 (1977).
[8] G. W. Ray, L. F. Keyser, and R. T. Watson, J. Phys. Chem. **84**, 1674 (1980).
[9] R. S. Lewis, S. P. Sander, S. Wagner, and R. T. Watson, J. Phys. Chem. **84**, 2009 (1980).
[10] O. Dobis and S. W. Benson, J. Am. Chem. Soc. **112**, 1023 (1990).
[11] G. Poulet, G. Laverdet, and G. Le Bras, J. Phys. Chem. **85**, 1892 (1981).

$Cl + C_3H_8 \rightarrow HCl + n\text{-}C_3H_7$ (1)
$\rightarrow HCl + i\text{-}C_3H_7$ (2)

$\Delta H^\circ(1)=-11.6$ kJ·mol−1
$\Delta H^\circ(2)=-19.1$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2$)

$k=1.4\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k=1.2\times10^{-10}\exp(40/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 220–600 K.

Reliability

$\Delta\log k=\pm0.12$ at 298 K.
$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is an average of the absolute rate coefficient of Lewis *et al.*[1] and the relative rate measurements of Pritchard *et al.*[2] Knox and Nelson,[3] Atkinson and Aschmann,[4] and Wallington *et al.*,[5] all of which are in reasonable agreement. The temperature dependence is that determined by Lewis *et al.*[1] The preferred values are identical to our previous evaluation, IUPAC, 1992.[6]

References

[1] R. S. Lewis, S. P. Sander, S. Wagner, and R. T. Watson, J. Phys. Chem. **84**, 2009 (1980).
[2] H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, J. Am. Chem. Soc. **77**, 2629 (1955).
[3] J. H. Knox and R. L. Nelson, Trans. Faraday Soc. **55**, 937 (1959).
[4] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).
[5] T. J. Wallington, L. M. Skewes, W. O. Siegl, C. H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + HCHO \rightarrow HCl + HCO$

$\Delta H° = -63.2\ kJ \cdot mol^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 7.3 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.
$k = 8.2 \times 10^{-11} \exp(-34/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 200–500 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred temperature dependence is based on a least-squares fit to the 200–500 K data of Michael *et al.*[1] and the 223–323 K data of Anderson and Kurylo.[2] The preferred 298 K rate coefficient is based on these absolute studies and the room temperature data of Niki *et al.*,[3] Fasano and Nogar,[4] and Poulet *et al.*,[5] all of which are in good agreement. The preferred values are identical to our previous evaluation, IUPAC, 1992.[6]

References

[1] J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, J. Chem. Phys. **70**, 1147 (1979).
[2] P. C. Anderson and M. J. Kurylo, J. Phys. Chem. **83**, 2053 (1979).
[3] H. Niki, P. D. Maker, L. P. Breitenbach, and C. M. Savage, Chem. Phys. Lett. **57**, 596 (1978).
[4] D. M. Fasano and N. S. Nogar, Int. J. Chem. Kinet. **13**, 325 (1981).
[5] G. Poulet, G. Laverdet, and G. Le Bras, J. Phys. Chem. **85**, 1892 (1981).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + CH_3CHO \rightarrow HCl + CH_3CO \quad (1)$
$\rightarrow HCl + CH_2CHO \quad (2)$

$\Delta H°(1) = -72.1\ kJ \cdot mol^{-1}$
$\Delta H°(2) = -35.2\ kJ \cdot mol^{-1}$

Rate coefficient data ($k = k_1 + k_2$)

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(9.2 \pm 0.7) \times 10^{-11}$	298±2	Scollard *et al.*, 1993[1]	(a)
Reviews and Evaluations			
7.2×10^{-11}	210–340	IUPAC, 1992[2]	(b)

Comments

(a) Relative rate method. Cl atoms were generated by the photolysis of Cl_2 in Cl_2-CH_3CHO-dimethyl ether-N_2 mixtures, and the concentrations of CH_3CHO and dimethyl ether measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio $k(Cl + CH_3CHO)/k(Cl + \text{dimethyl ether})$ is placed on an absolute basis by using a rate coefficient of $k(Cl + \text{dimethyl ether}) = 1.76 \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$.[3]

(b) See Comments on Preferred Values.

Preferred Values

$k = 7.2 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$, independent of temperature over the range 210–340 K.
$k_2/k < 0.05$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute rate coefficient of Payne *et al.*[4] and the relative rate coefficients of Niki *et al.*,[5] Wallington *et al.*,[6] and Bartels *et al.*[7] The lack of a temperature dependence of the rate coefficient is consistent with the data of Payne *et al.*[4] The branching ratio is derived from the data of Niki *et al.*[5] and Bartels *et al.*[7] The relative rate coefficient of Scollard *et al.*[1] is ~30% higher than the preferred values, which are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, J. Phys. Chem. **97**, 4683 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, J. Chem. Phys. **70**, 3652 (1979).
[4] W. A. Payne, D. F. Nava, F. L. Nesbitt, and L. J. Stief, J. Phys. Chem. **94**, 7190 (1990).
[5] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **89**, 588 (1985).
[6] T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).
[7] M. Bartels, K. Hoyermann, and U. Lange, Ber. Bunsenges Phys. Chem. **93**, 423 (1989).

$Cl + C_2H_5CHO \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the relative rate study of Wallington *et al.*,[1] with expanded uncertainty limits, and is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + CH_3COCH_3 \rightarrow HCl + CH_3COCH_2$

$\Delta H^\circ = -20.3$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 3.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the relative rate study of Wallington *et al.*,[1] with expanded uncertainties, and is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + CH_3OH \rightarrow HCl + CH_2OH$

$\Delta H^\circ = -21.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.14 \pm 0.67) \times 10^{-11}$	298±2	Dóbé *et al.*, 1993[1]	(a)
Relative Rate Coefficients			
$(5.3 \pm 1.2) \times 10^{-11}$	248-573	Lightfoot *et al.*, 1990[2]	(b)
Reviews and Evaluations			
5.3×10^{-11}	200–500	IUPAC, 1992[3]	(c)
5.4×10^{-11}	200–500	NASA, 1994[4]	(d)

Comments

(a) Discharge flow system with EPR detection of Cl atoms.

(b) Derived from the measured initial HO_2 and CH_3O_2 radical concentrations in flash photolyzed Cl_2-CH_3OH-CH_4-N_2-O_2 mixtures, with the HO_2 and CH_3O_2 concentrations being measured by time-resolved UV absorption. Placed on an absolute basis by use of $k(Cl + CH_4)=9.6\times10^{-12} \exp(-1350/T)$ cm^3 $molecule^{-1}$ s^{-1} (this evaluation).

(c) The 298 K rate coefficient was the average of the rate coefficients of Michael *et al.*,[5] Wallington *et al.*,[6] and Nelson *et al.*[7] The zero temperature dependence was taken from the study of Michael *et al.*[5]

(d) Based on the absolute rate coefficients of Michael *et al.*,[5] Payne *et al.*,[8] and Dóbé *et al.*,[1] and the relative rate coefficients of Wallington *et al.*,[6] Nelson *et al.*,[7] and Lightfoot *et al.*[2]

Preferred Values

$k=5.5\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, independent of temperature over the range 200–573 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.

$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The preferred 298 K value is the average of the rate coefficients of Michael *et al.*,[5] Wallington *et al.*,[6] Nelson *et al.*,[7] Lightfoot *et al.*,[2] and Dóbé *et al.*,[1] and is in excellent agreement with the absolute rate coefficient of $(5.1\pm1.0)\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K determined by Payne *et al.*[8] for the reaction $Cl + CH_3OD \rightarrow HCl + CH_2OD$. The zero temperature dependence is taken from the studies of Michael *et al.*[5] and Lightfoot *et al.*[2]

References

[1] S. Dóbé, M. Otting, F. Temps, H. Gg. Wagner, and H. Ziemer, Ber. Bunsenges. Phys. Chem. **97**, 877 (1993).

[2] P. D. Lightfoot, B. Veyret, and R. Lesclaux, J. Phys. Chem. **94**, 708 (1990).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] NASA Evaluation No. 10, 1994 (see references in Introduction).

[5] J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, J. Chem. Phys. **70**, 3652 (1979).

[6] T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).

[7] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

[8] W. A. Payne, J. Brunning, M. B. Mitchell, and L. J. Stief, Int. J. Chem. Kinet. **20**, 63 (1988).

$Cl + C_2H_5OH \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=9.4\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of those of Wallington *et al.*[1] and Nelson *et al.*,[2] which are in good agreement, and is identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).

[2] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + n\text{-}C_3H_7OH \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=1.5\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the data of Wallington *et al.*[1] and Nelson *et al.*,[2] which are in excellent agreement, and is identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).

[2] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

Cl + *i*-C_3H_7OH → products

No new data have been published since our last evaluation.

Preferred Values

$k=8.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the relative rate study of Nelson *et al.*,[1] and is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + CH_3OOH \rightarrow HCl + CH_3O_2$ (1)

$\rightarrow HCl + CH_2OOH$ (2)

$\Delta H°(1)=-72$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2$)

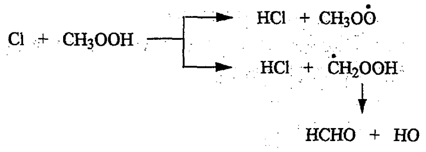
$k=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.5$ at 298 K.

Comments on Preferred Values

The only study carried out to date is that of Wallington *et al.*[1] The reaction may occur by the two pathways,



and the formation of HO radicals may have led to secondary reactions involving HO radicals. Since the room-temperature rate coefficient for the Cl atom reaction with H_2O_2 (this evaluation) is two orders of magnitude lower than that for Cl + CH_3OOH, it is expected that channel (2) will dominate. Wallington *et al.*[1] concluded that secondary reactions involving HO radicals did not contribute ≥15% to the observed CH_3OOH consumption. The cited uncertainty limits on the preferred values reflect this possibility of HO radical involvement in the Wallington *et al.*[1] study. The preferred value is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + HCOOH \rightarrow HCl + HCO_2$ (1)
$\rightarrow HCl + COOH$ (2)

$\Delta H^\circ(2) = -58$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2$)

$k=2.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the rate coefficients obtained by Wallington *et al.*[1] relative to $k(Cl + CH_3Cl)$ and $k(Cl + CH_4)$, which are in good agreement, and is identical to our previous evaluation, IUPAC, 1992.[2]

Tyndall *et al.*[3] have observed that CO_2 is the sole carbon-containing product formed from this reaction in air or N_2 diluent, and conclude from comparison of the rate coefficients for the reactions of the Cl atom with HCOOH, CH_3COOH,[4] and CD_3COOH[4] that reaction channel (2) dominates.

References

[1] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] G. S. Tyndall, T. J. Wallington, and A. R. Potts, Chem. Phys. Lett. **186**, 149 (1991).

[4] S. Koch and G. K. Moortgat, Chem. Phys. Lett. **173**, 531 (1990).

$Cl + CH_3COOH \rightarrow HCl + CH_2COOH$ (1)
$\rightarrow HCl + CH_3COO$ (2)

$\Delta H^\circ(2) = 10.9$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2$)

$k=2.8\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole study of Koch and Moortgat,[1] and is identical to our previous evaluation, IUPAC, 1992.[2] The measured rate coefficient ratio of $k(Cl + CH_3COOH)/k(Cl + CD_3COOH)=3.7$ at 298 ±1 K[1] indicates that channel (1) dominates at 298 K.

References

[1] S. Koch and G. K. Moortgat, Chem. Phys. Lett. **173**, 531 (1990).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + CH_3ONO_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=2.4\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the relative rate study of Nielsen *et al.*,[1] and is identical to our previous evaluation, IUPAC, 1992.[2] The reaction probably occurs via H-atom abstraction from the -CH_3 group.[1]

References

[1] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + C_2H_5ONO_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=4.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the data of Wallington *et al.*[1] and Nielsen *et al.*,[2] and is identical to our previous evaluation, IUPAC, 1992.[3] The reaction probably proceeds by H-atom abstraction from the C-H bonds.[2]

References

[1] T. J. Wallington, M. M. Hinman, J. M Andino, W. O. Siegl, and S. M. Japar, Int. J. Chem. Kinet. **22**, 665 (1990).
[2] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + n\text{-}C_3H_7ONO_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=2.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the data of Wallington *et al.*[1] and Nielsen *et al.*,[2] and is identical to our previous evaluation, IUPAC, 1992.[3] The reaction probably proceeds by H-atom abstraction from the C-H bonds.[2]

References

[1] T. J. Wallington, M. M. Hinman, J. M. Andino, W. O. Siegl, and S. M. Japar, Int. J. Chem. Kinet. **22**, 665 (1990).
[2] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1990).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + i\text{-}C_3H_7ONO_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=5.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole study of Wallington *et al.*,[1] and is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] T. J. Wallington, M. M. Hinman, J. M. Andino, W. O. Siegl, and S. M. Japar, Int. J. Chem. Kinet. **22**, 665 (1990).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + CH_3C(O)OONO_2 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k < 2\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the relative rate coefficient measurement of Wallington *et al.*,[1] in which no reaction of $CH_3C(O)OONO_2$ was observed in the presence of Cl atoms. In both the relative rate study of Wallington *et al.*[1] and the absolute rate study of Tsalkani *et al.*,[2] the major impurity in the $CH_3C(O)OONO_2$ samples would be the C_{12} or C_{13} alkane solvent, respectively. While this was of no consequence in the relative rate study of Wallington *et al.*,[1] the presence of ~0.1% tridecane in the $CH_3C(O)OONO_2$ sample used by Tsalkani *et al.*[2] could account for the Cl reaction rate observed; their $CH_3C(O)OONO_2$ sample was >99% pure from IR measurements. The upper limit cited here is a factor of ~3 higher than measured by Wallington *et al.*[1] to allow for higher uncertainties, and is identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

[2] N. Tsalkani, A. Mellouki, G. Poulet, G. Toupance, and G. Le Bras, J. Atmos. Chem. **7**, 409 (1988).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + CH_3CN \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k \leq 2\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the upper limit to the rate coefficient determined by Kurylo and Knable,[1] and is identical to our previous evaluation, IUPAC, 1992.[2] The low temperature ($\leq$410 K) rate coefficient data of Poulet *et al.*[3] could have been influenced by a heterogeneous reaction. The rate coefficients of Olbregts *et al.*[4] at 370 and 413 K are in good agreement with the higher temperature data of Poulet *et al.*[3]

References

[1] M. J. Kurylo and G. L. Knable, J. Phys. Chem. **88**, 3305 (1984).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] G. Poulet, G. Laverdet, J. L. Jourdain, and G. Le Bras, J. Phys. Chem. **88**, 6259 (1984).

[4] J. Olbregts, G. Brasseur, and E. Arijs, J. Photochem. **24**, 315 (1984).

$Cl + HC(O)Cl \rightarrow HCl + ClCO$

No new data have been published since our last evaluation.

Preferred Values

$k = 7.8\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.2\times10^{-11} \exp(-815/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 265–325 K.

Reliability

$\Delta\log k = \pm0.15$ at 298 K.
$\Delta(E/R) = \pm300$ K.

Comments on Preferred Values

At 298 K, the rate coefficients of Niki *et al.*[1] and Libuda *et al.*[2] are in excellent agreement and are in reasonably good agreement with the 305 K rate coefficient data of Sanhueza and Heicklen.[3] The preferred 298 K rate coefficient is that of Niki *et al.*[1] and Libuda *et al.*,[2] and the temperature dependence is that derived from the study of Libuda *et al.*[2] The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **12**, 915 (1980).

[2] H. G. Libuda, F. Zabel, E. H. Fink, and K. H. Becker, J. Phys. Chem. **94**, 5860 (1990).

[3] E. Sanhueza and J. Heicklen, J. Phys. Chem. **79**, 7 (1975).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + CH_3F$ (HFC-41) → $HCl + CH_2F$

$\Delta H° = -12.8\ kJ \cdot mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.8\times10^{-12}\exp[-(770\pm55)/T]$	216–296	Manning and Kurylo, 1977[1]	(a)
3.6×10^{-13}	298		
Relative Rate Coefficients			
$1.9\times10^{-11}\exp(-1160/T)$	273-368	Tschuikow-Roux *et al.*, 1988[2]	(b)
3.8×10^{-13}	298		
$(3.4\pm0.7)\times10^{-13}$	298	Tuazon, Atkinson, and Corchnoy, 1992[3]	(c)
$(3.24\pm0.51)\times10^{-13}$	298	Wallington *et al.*, 1992[4]	(d)
Reviews and Evaluations			
$2.0\times10^{-11}\exp(-1200/T)$	200–300	NASA, 1994[5]	(e)

Comments

(a) Flash photolysis system with resonance fluorescence detection of Cl atoms.

(b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC and the measured rate coefficient ratios are placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 9.6\times10^{-12} \times\exp(-1350/T)\ cm^3\ molecule^{-1}\ s^{-1}$ (this evaluation).

(c) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FT-IR spectroscopy. The measured rate coefficient is placed on absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0\times10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ (this evaluation).

(d) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by IR absorption. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0\times10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ (this evaluation).

(e) Based on the results of Tschuikow-Roux *et al.*,[2] Tuazon *et al.*,[3] and Wallington *et al.*[4]

Preferred Values

$k = 3.5\times10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k = 1.7\times10^{-11}\exp(-1160/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 273–368 K.

Reliability

$\Delta\log k = \pm0.15$ at 298 K.

$\Delta(E/R) = \pm500$ K.

Comments on Preferred Values

The recommended value is based on results of the temperature-dependent relative rate study of Tschuikow-Roux *et al.*[2] and the relative rate studies of Tuazon *et al.*[3] and Wallington *et al.*[4] The results of the absolute rate study of Manning and Kurylo[1] are in good agreement at room temperature but show a weaker temperature dependence, which is encompassed within the error limits.

References

[1] R. G. Manning and M. J. Kurylo, J. Phys. Chem. **81**, 291 (1977).

[2] E. Tschuikow-Roux, F. Faraji, S. Paddison, J. Niedzielski, and K. Miyokawa, J. Phys. Chem. **92**, 1488 (1988).

[3] E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, Int. J. Chem. Kinet. **24**, 639 (1992).

[4] T. J. Wallington, J. C. Ball, O. J. Nielsen, and E. Bartkiewicz, J. Phys. Chem. **96**, 1241 (1992).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$

$\Delta H° = -9.8\ kJ \cdot mol^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 4.9\times10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k = 3.3\times10^{-11}\exp(-1250/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 233–322 K.

Reliability

$\Delta\log k = \pm0.15$ at 298 K.

$\Delta(E/R) = \pm300$ K.

Comments on Preferred Values

At 298 K, the absolute rate coefficients of Clyne and Walker[1] and Manning and Kurylo[2] and the relative rate coefficient of Wallington *et al.*[3] are in good agreement. However, the temperature dependencies measured by Clyne and Walker[1] and Manning and Kurylo[2] do not agree. The preferred 298 K rate coefficient is the average of those of Manning and Kurylo[2] and Wallington *et al.*,[3] and the temperature dependence is that of Manning and Kurylo.[2] The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] M. A. A. Clyne and R. F. Walker, J. Chem. Soc. Faraday Trans. 1, **69**, 1547 (1973).

[2] R. G. Manning and M. J. Kurylo, J. Phys. Chem. **81**, 291 (1977).

[3] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + CH_2F_2(HFC\text{-}32) \rightarrow HCl + CHF_2$

$\Delta H° = 0.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$1.5\times10^{-11}\exp(-1580/T)$	281–368	Tschuikow-Roux, Yano, and Niedzielski, 1985[1]	(a)
7.3×10^{-14}	298		
Reviews and Evaluations			
$1.7\times10^{-11}\exp(-1630/T)$	281–368	NASA, 1994[2]	(b)

Comments

(a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC and the measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient $k(Cl + CH_4) = 9.6\times10^{-12}\exp(-1350/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Based on the results of Tschuikow-Roux *et al.*[1]

Preferred Values

$k = 7.3\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.5\times10^{-11}\exp(-1580/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 281–368 K.

Reliability

$\Delta\log k = \pm0.5$ at 298 K.

$\Delta(E/R) = \pm500$ K.

Comments on Preferred Values

The recommended value is based on the results of the relative rate study of Tschuikow-Roux *et al.*,[1] normalized to the value of the rate constant for the reference reaction ($Cl + CH_4$) recommended in this evaluation.

References

[1] E. Tschuikow-Roux, T. Yano, and J. Niedzielski, J. Chem. Phys. **82**, 65 (1985).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CH_2FCl$ (HCFC-31) → $HCl + CHFCl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$1.8\times10^{-11}\exp(-1340/T)$	273–368	Tschuikow-Roux *et al.*, 1988[1]	(a)
2.0×10^{-13}	298		
$(1.10\pm0.25)\times10^{-13}$	298	Tuazon, Atkinson, and Corchnoy, 1992[2]	(b)
Reviews and Evaluations			
$1.2\times10^{-11}\exp(-1390/T)$	273–368	NASA, 1994[3]	(c)

Comments

(a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC, and the measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4)=9.6\times10^{-12}\exp(-1350/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Relative rate technique. Cl atoms were generated by photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on absolute basis by use of a rate coefficient of $k(Cl + CH_4)=1.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Based on the room temperature results of Tuazon *et al.*[2] and the temperature dependent results of Tschuikow-Roux *et al.*[1]

Preferred Values

$k=1.1\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.0\times10^{-11}\exp(-1340/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 273–368 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The recommended value is based on the room temperature results of Tuazon *et al.*[2] and the temperature dependence reported by Tschuikow-Roux *et al.*,[1] normalized to the value of the rate constant for the reference reaction ($Cl + CH_4$) recommended in this evaluation.

References

[1] E. Tschuikow-Roux, F. Faraji, S. Paddison, J. Niedzielski, and K. Miyokawa, J. Phys. Chem. **92**, 1488 (1988).
[2] E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, Int. J. Chem. Kinet. **24**, 639 (1992).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$

$\Delta H^\circ=-19.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$2.70\times10^{-11}\exp[-(1301\pm2)/T]$	273–368	Tschuikow-Roux *et al.*, 1988[1]	(a)
3.43×10^{-13}	298		
Reviews and Evaluations			
$8.7\times10^{-12}\exp(-910/T)$	270–330	IUPAC, 1992[2]	(b)
$3.1\times10^{-11}\exp(-1350/T)$	273–368	NASA, 1994[3]	(c)

Comments

(a) Relative rate method. Cl atoms were generated by the photolysis of Cl_2 at 424 nm, and the concentrations of CH_2Cl_2 and CH_4 measured by GC. The measured rate coefficient ratio of $k(Cl + CH_2Cl_2)/k(Cl + CH_4) =(2.81\pm0.02)\exp[-(49\pm2)/T]$ is placed on an absolute basis by using the rate coefficient of $k(Cl + CH_4)=9.6\times10^{-12}\exp(-1350/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) The 298 K rate coefficient was based on the relative rate coefficients of Knox[4] and Niki *et al.*,[5] and the temperature dependence was derived from the study of Knox.[4]

(c) Based on the relative rate coefficients of Tschuikow-Roux *et al.*[1]

Preferred Values

$k=3.6\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=2.8\times10^{-11}\exp(-1300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–370 K.

Reliability
$\Delta\log k=\pm0.15$ at 298 K.
$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The reported rate coefficient data[1,4–7] exhibit appreciable scatter in both the room temperature rate coefficients as well as in the temperature dependencies. At room temperature, the rate coefficients derived from the most recent relative rate studies of Niki *et al.*[5] and Tschuikow-Roux *et al.*[1] are in good agreement. Accordingly, the preferred 298 K rate coefficient is the average of those of Niki *et al.*[5] and Tschuikow-Roux *et al.*,[1] with the temperature dependence being that derived from the data of Tschuikow-Roux *et al.*[1] Analogous to the Cl + CH_4 reaction, the room temperature rate coefficients of Davis *et al.*[6] and Clyne and Walker[7] and the temperature dependence of Clyne and Walker[7] are higher than the preferred values.

References

[1] E. Tschuikow-Roux, F. Faraji, S. Paddison, J. Niedzielski, and K. Miyokawa, J. Phys. Chem. **92**, 1488 (1988).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA, Evaluation No. 11, 1994 (see references in Introduction).
[4] J. H. Knox, Trans. Faraday Soc. **58**, 275 (1962).
[5] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **12**, 1001 (1980).
[6] D. D. Davis, W. Braun, and A. M. Bass, Int. J. Chem. Kinet. **2**, 101 (1970).
[7] M. A. A. Clyne and R. F. Walker, J. Chem. Soc. Faraday Trans. 1, **69**, 1547 (1973).

Cl + CHF_2Cl (HCFC-22) → HCl + CF_2Cl

$\Delta H^\circ=-9.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.7\pm0.2)\times10^{-15}$	297	Sawerysyn *et al.*, 1992[1]	(a)
Relative Rate Coefficients			
$(2.0\pm0.4)\times10^{-15}$	298	Tuazon, Atkinson, and Corchnoy, 1992[2]	(b)
Reviews and Evaluations			
1.9×10^{-15}	298	NASA, 1994[3]	(c)

Comments

(a) Discharge flow system with MS monitoring of pseudo-first-order decay of the haloalkane in the presence of excess Cl atoms.

(b) Relative rate technique. Cl atoms were generated by photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Based on the results of Sawerysyn *et al.*[1] and Tuazon *et al.*[2]

Preferred Values

$k=1.9\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta\log k=\pm0.15$ at 298 K.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported by Sawerysyn *et al.*[1] and Tuazon *et al.*,[2] which are in good agreement. Since the only studies carried out have been at room temperature, only a room temperature value is recommended.

References

[1] J. P. Sawerysyn, A. Talhaoui, B. Meriaux, and P. Devolder, Chem. Phys. Lett. **198**, 197 (1992).
[2] E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, Int. J. Chem. Kinet. **24**, 639 (1992).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CHFCl_2(HCFC\text{-}21) \rightarrow HCl + CFCl_2$

$\Delta H° = -17.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.0\pm0.2)\times10^{-14}$	294	Glavas and Heicklen, 1985[1]	(a)
$(2.1\pm0.4)\times10^{-14}$	298	Tuazon, Atkinson, and Corchnoy, 1992[2]	(b)
Reviews and Evaluations			
2.1×10^{-14}	298	NASA, 1994[3]	(c)

Comments

(a) Relative rate technique employing steady-state photolysis of Cl_2-$CHFCl_2$-O_2-NO-NO_2-N_2 mixtures. The measured rate coefficient ratio is placed on absolute basis by use of a rate coefficient of $k(Cl + NO + M) = 1.0\times10^{-31}$ cm^6 molecule^{-2} s^{-1}.

(b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Based on the results of Tuazon *et al.*[2]

Preferred Values

$k = 2.1\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm0.3$ at 298 K.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported by Tuazon *et al.*[2] These results are preferred over the earlier, less direct results of Glavas and Heicklen.[1] Since the only studies carried out have been at room temperature, only a room temperature value is recommended.

References

[1] S. Glavas and J. Heicklen, J. Photochem. **31**, 21 (1985).

[2] E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, Int. J. Chem. Kinet. **24**, 639 (1992).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CHCl_3 \rightarrow HCl + CCl_3$

$\Delta H° = -39.2$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 7.6\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.9\times10^{-12}\exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–330 K.

Reliability

$\Delta \log k = \pm0.3$ at 298 K.

$\Delta(E/R) = \pm400$ K.

Comments on Preferred Values

The preferred values are based on the relative rate study of Knox,[1] with the uncertainty limits being sufficient to encompass the data of Clyne and Walker.[2] The preferred values are identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] J. H. Knox, Trans. Faraday Soc. **58**, 275 (1962).

[2] M. A. A. Clyne and R. F. Walker, J. Chem. Soc., Faraday Trans. 1, **69**, 1547 (1973).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + CH_3CH_2F(HFC-161) \rightarrow HCl + CH_3CHF$ (1)
$\rightarrow HCl + CH_2CH_2F$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$k_1=1.5\times10^{-11}\exp(-240/T)$	281–368	Tschuikow-Roux, Yano, and Niedzielski, 1985[1]	(a)
$k_1=6.7\times10^{-12}$	298		
$k_2=1.2\times10^{-11}\exp(-830/T)$	281–368		
$k_2=7.3\times10^{-13}$	298		
Reviews and Evaluations			
$k_1=1.8\times10^{-11}\exp(-290/T)$	281–368	NASA, 1994[2]	(b)
$k_2=1.4\times10^{-11}\exp(-880/T)$	281–368		

Comments

(a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC and the measured rate coefficient ratios are placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4)=9.6\times10^{-12}\exp(-1350/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Based on the results of Tschuikow-Roux *et al.*[1]

Preferred Values

$k_1=6.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1=1.5\times10^{-11}\exp(-240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 281–368 K.

$k_2=7.3\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2=1.2\times10^{-11}\exp(-830/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 281–368 K.

Reliability

$\Delta\log k_1=\Delta\log k_2=\pm0.5$ at 298 K.

$\Delta(E_1/R)=\Delta(E_2/R)=\pm500$ K.

Comments on Preferred Values

The recommended values are based on the results of the relative rate study of Tschuikow-Roux *et al.*,[1] normalized to the value of the rate constant for the reference reaction ($Cl + CH_4$) recommended in this evaluation.

References

[1] E. Tschuikow-Roux, T. Yano, and J. Niedzielski, J. Chem. Phys. **82**, 65 (1985).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CH_3CHF_2(HFC-152a) \rightarrow HCl + CH_3CF_2$ (1)
$\rightarrow HCl + CH_2CHF_2$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$k_1=6.8\times10^{-12}\exp(-960/T)$	280–360	Yano and Tschuikow-Roux, 1986[1]	(a)
$k_1=2.7\times10^{-13}$	298		
$k_2=7.6\times10^{-12}\exp(-2394/T)$	280–360		
$k_2=2.5\times10^{-15}$	298		
$(2.4\pm0.7)\times10^{-13}$	295	Wallington and Hurley, 1992[2]	(b)
$(2.4\pm0.5)\times10^{-13}$	298	Tuazon, Atkinson, and Corchnoy, 1992[3]	(c)
Reviews and Evaluations			
$k_1=6.4\times10^{-12}\exp(-950/T)$	280–360	NASA, 1994[4]	(d)
$k_2=7.2\times10^{-12}\exp(-2390/T)$	280–360		

Comments

(a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC and the measured rate coefficient ratios are placed on an absolute basis by use of a rate coefficient of $k(Cl + C_2H_6) = 8.1 \times 10^{-11} \exp(-95/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Based on the results of Yano and Tschuikow-Roux.[1] The room temperature values of Refs. 2 and 3 are in good agreement.

Preferred Values

$k_1 = 2.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 6.8 \times 10^{-12} \exp(-960/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280–360 K.

$k_2 = 2.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2 = 7.6 \times 10^{-12} \exp(-2395/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280–360 K.

Reliability

$\Delta \log k_1 = \pm 0.15$ at 298 K.

$\Delta \log k_2 = \pm 0.5$ at 298 K.

$\Delta(E_1/R) = \Delta(E_2/R) = \pm 500$ K.

Comments on Preferred Values

The recommended values for the two reaction channels are based on the results of the relative rate study of Yano and Tschuikow-Roux,[1] normalized to the value of the rate constant for the reference reaction ($Cl + C_2H_6$) recommended in this evaluation. The overall rate coefficient is in good agreement with the room temperature relative rate coefficient studies of Wallington and Hurley[2] and Tuazon *et al.*[3]

References

[1] T. Yano and E. Tschuikow-Roux, J. Photochem. **32**, 25 (1986).
[2] T. J. Wallington and M. D. Hurley, Chem. Phys. Lett. **189**, 437 (1992).
[3] E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, Int. J. Chem. Kinet. **24**, 639 (1992).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CH_2FCH_2F$(HFC-152) → $HCl + CHFCH_2F$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$2.7 \times 10^{-11} \exp(-1060/T)$	280–360	Yano and Tschuikow-Roux, 1986[1]	(a)
7.7×10^{-13}	298		
Reviews and Evaluations			
$2.6 \times 10^{-11} \exp(-1060/T)$	280–360	NASA, 1994[2]	(b)

Comments

(a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC and the measured rate coefficient ratios are placed on an absolute basis by use of a rate coefficient of $k(Cl + C_2H_6) = 8.1 \times 10^{-11} \exp(-95/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Based on the results of Yano and Tschuikow-Roux.[1]

Preferred Values

$k = 7.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.7 \times 10^{-11} \exp(-1060/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280–360 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The recommended value is based on the results of the relative rate study of Yano and Tschuikow-Roux,[1] normalized to the value of the rate constant for the reference reaction ($Cl + C_2H_6$) recommended in this evaluation.

References

[1] T. Yano and E. Tschuikow-Roux, J. Photochem. **32**, 25 (1986).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CH_3CF_3(HFC\text{-}143a) \rightarrow HCl + CH_2CF_3$

$\Delta H° = 18.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$1.0\times10^{-11}\exp(-3830/T)$	281–368	Tschuikow-Roux, Yano, and Niedzielski, 1985[1]	(a)
2.6×10^{-17}	298		
Reviews and Evaluations			
$1.2\times10^{-11}\exp(-3880/T)$	281–368	NASA, 1994[2]	(b)

Comments

(a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC and the measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 9.6\times10^{-12}\exp(-1350/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Based on the results of Tschuikow-Roux *et al.*[1]

Preferred Values

$k = 2.6\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.0\times10^{-11}\exp(-3830/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 281–368 K.

Reliability

$\Delta\log k = \pm0.5$ at 298 K.

$\Delta(E/R) = \pm500$ K.

Comments on Preferred Values

The recommended value is based on the results of the relative rate study of Tschuikow-Roux *et al.*,[1] normalized to the value of the rate constant for the reference reaction ($Cl + CH_4$) recommended in this evaluation.

References

[1] E. Tschuikow-Roux, T. Yano, and J. Niedzielski, J. Chem. Phys. **82**, 65 (1985).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CH_2FCHF_2(HFC\text{-}143) \rightarrow HCl + CH_2FCF_2 \quad (1)$
$\rightarrow HCl + CHFCHF_2 \quad (2)$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$k_1 = 4.8\times10^{-12}\exp(-1560/T)$	281–368	Tschuikow-Roux, Yano, and Niedzielski, 1985[1]	(a)
$k_1 = 2.5\times10^{-14}$	298		
$k_2 = 6.7\times10^{-12}\exp(-1670/T)$	281–368		
$k_2 = 2.5\times10^{-14}$	298		
Reviews and Evaluations			
$k_1 = 5.5\times10^{-12}\exp(-1610/T)$	281–368	NASA, 1994[2]	(b)
$k_2 = 7.7\times10^{-12}\exp(-1720/T)$	281–368		

Comments

(a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC and the measured rate coefficient ratios are placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 9.6\times10^{-12}\exp(-1350/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Based on the results of Tschuikow-Roux *et al.*[1]

Preferred Values

$k_1 = 2.5\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 4.8\times10^{-12}\exp(-1560/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 281–368 K.

$k_2 = 2.5\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2=6.7\times10^{-12}\exp(-1670/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 281–368 K.

Reliability

$\Delta\log k_1=\Delta\log k_2=\pm0.5$ at 298 K.
$\Delta(E/R)_1=\Delta(E/R)_2=\pm500$ K.

Comments on Preferred Values

The recommended values are based on the results of the relative rate study of Tschuikow-Roux *et al.*,[1] normalized to the value of the rate constant for the reference reaction (Cl + CH_4) recommended in this evaluation.

References

[1] E. Tschuikow-Roux, T. Yano, and J. Niedzielski, J. Chem. Phys. **82**, 65 (1985).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

Cl + CH_3CF_2Cl(HCFC-142b) → HCl + CH_2CF_2Cl

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.6\pm2.0)\times10^{-16}$	297	Sawerysyn *et al.*, 1992[1]	(a)
Relative Rate Coefficients			
$(3.90\pm0.52)\times10^{-16}$	295	Wallington and Hurley, 1992[2]	(b)
$(3.7\pm0.8)\times10^{-16}$	298	Tuazon, Atkinson, and Corchnoy, 1992[3]	(c)
Reviews and Evaluations			
4.0×10^{-16}	298	NASA, 1994[4]	(d)

Comments

(a) Discharge flow system with MS monitoring of the pseudo-first-order decays of the haloalkane in the presence of excess Cl atoms.

(b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(Cl + CH_4)$=1.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of k(Cl + CH_4)$=1.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Based on the results of Sawerysyn *et al.*,[1] Wallington and Hurley,[2] and Tuazon *et al.*[3]

Preferred Values

$k=4.0\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported in Refs. 1–3, which are in good agreement. Since studies have only been carried out at room temperature, no temperature dependence is recommended.

References

[1] J. P. Sawerysyn, A. Talhaoui, B. Meriaux, and P. Devolder, Chem. Phys. Lett. **198**, 197 (1992).
[2] T. J. Wallington and M. D. Hurley, Chem. Phys. Lett. **189**, 437 (1992).
[3] E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, Int. J. Chem. Kinet. **24**, 639 (1992).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CH_3CFCl_2(HCFC\text{-}141b) \rightarrow HCl + CH_2CFCl_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.1\pm0.2)\times10^{-15}$	297	Sawerysyn *et al.*, 1992[1]	(a)
$1.0\times10^{-12}\exp[-(1800\pm500)/T]$	298–376	Warren and Ravishankara, 1993[2]	(b)
$(2.4\pm0.4)\times10^{-15}$	298		
Relative Rate Coefficients			
$(2.0\pm0.2)\times10^{-15}$	295	Wallington and Hurley, 1992[3]	(c)
$(2.4\pm0.5)\times10^{-15}$	298	Tuazon, Atkinson, and Corchnoy, 1992[4]	(d)
Reviews and Evaluations			
$1.0\times10^{-12}\exp(-1800/T)$	298–376	NASA, 1994[5]	(e)

Comments

(a) Discharge flow system with MS monitoring of the pseudo-first-order decays of the haloalkane in the presence of excess Cl atoms.

(b) Cl atoms were generated by laser flash photolysis of CCl_4 at 222 nm. The pseudo-first-order decays of Cl atoms in excess HCFC were monitored by resonance fluorescence.

(c) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) Based on the results of Refs. 1–4.

Preferred Values

$k=2.3\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.0\times10^{-12}\exp(-1800/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 298–376 K.

Reliability

$\Delta\log k = \pm0.1$ at 298 K.

$\Delta(E/R) = \pm500$ K.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported in Refs. 1–4, which are in good agreement. The recommended temperature dependence is that reported by Warren and Ravishankara,[2] the only study carried out over a range of temperatures. The reported A factor is lower than expected.

References

[1] J. P. Sawerysyn, A. Talhaoui, B. Meriaux, and P. Devolder, Chem. Phys. Lett. **198**, 197 (1992).

[2] R. F. Warren and A. R. Ravishankara, Int. J. Chem. Kinet. **25**, 833 (1993).

[3] T. J. Wallington and M. D. Hurley, Chem. Phys. Lett. **189**, 437 (1992).

[4] E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, Int. J. Chem. Kinet. **24**, 639 (1992).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CH_3CCl_3 \rightarrow HCl + CH_2CCl_3$

No new data have been published since our last evaluation.

Preferred Values

$k<4\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the study of Wine *et al.*,[1] and is identical to our previous evaluation, IUPAC, 1992.[2]

This reaction is too slow to be of importance in atmospheric chemistry.

References

[1] P. H. Wine, D. H. Semmes, and A. R. Ravishankara, Chem. Phys. Lett. **90**, 128 (1982).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Cl + CH_2FCF_3$(HFC-134a) → $HCl + CHFCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.6\pm0.3)\times10^{-15}$	297	Sawerysyn *et al.*, 1992[1]	(a)
Relative Rate Coefficients			
$(1.38\pm0.18)\times10^{-15}$	295	Wallington and Hurley, 1992[2]	(b)
$(1.6\pm0.3)\times10^{-15}$	298	Tuazon, Atkinson, and Corchnoy, 1992[3]	(c)
Reviews and Evaluations			
1.5×10^{-15}	298	NASA, 1994[4]	(d)

Comments

(a) Discharge flow system with MS monitoring of the pseudo-first-order decays of the haloalkane in the presence of excess Cl atoms.

(b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0\times10\ ^{13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Based on the results of Sawerysyn *et al.*,[1] Wallington and Hurley,[2] and Tuazon *et al.*[3]

Preferred Values

$k = 1.5\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.1$ at 298 K.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported in Refs. 1–3, which are in good agreement. Since studies have only been carried out at room temperature, no temperature dependence is recommended.

References

[1] J. P. Sawerysyn, A. Talhaoui, B. Meriaux, and P. Devolder, Chem. Phys. Lett. **198**, 197 (1992).
[2] T. J. Wallington and M. D. Hurley, Chem. Phys. Lett. **189**, 437 (1992).
[3] E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, Int. J. Chem. Kinet. **24**, 639 (1992).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CHF_2CHF_2$(HFC-134) → $HCl + CF_2CHF_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$8.7\times10^{-12}\exp(-2439/T)$	280–360	Yano and Tschuikow-Roux, 1986[1]	(a)
2.4×10^{-15}	298		
1.9×10^{-15}	298	Nielsen *et al.*, 1992[2]	(b)
Reviews and Evaluations			
$7.5\times10^{-12}\exp(-2430/T)$	280–360	NASA, 1994[3]	(c)

Comments

(a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Cl + C_2H_6) = 8.1\times10^{-11}\exp(-95/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Based on the results of Yano and Tschuikow-Roux *et al.*[1] and Nielsen *et al.*[2]

Preferred Values

$k = 2.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.9 \times 10^{-12} \exp(-2440/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280–360 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The recommended value is based on results of the relative rate studies of Nielsen *et al.*[2] and Yano and Tschuikow-Roux *et al.*[1] (the latter data being normalized to the value of the rate constant for the reference reaction ($Cl + C_2H_6$) recommended in this evaluation).

References

[1] T. Yano and E. Tschuikow-Roux, J. Photochem. **32**, 25 (1986).

[2] O. J. Nielsen, T. Ellermann, J. Sehested, and T. J. Wallington, J. Phys Chem. **96**, 10875 (1992).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CHF_2CF_3$(HFC-125) → $HCl + CF_2CF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(2.4 \pm 0.5) \times 10^{-16}$	298	Tuazon, Atkinson, and Corchnoy, 1992[1]	(a)
$(2.5 \pm 0.6) \times 10^{-16}$	295	Sehested *et al.*, 1993[2]	(b)
Reviews and Evaluations			
2.4×10^{-16}	298	NASA, 1994[3]	(c)

Comments

(a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is ratio placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_3CF_2Cl) = 4.0 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Based on the results of Tuazon *et al.*[1] and Sehested *et al.*[2]

Preferred Values

$k = 2.4 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred value at 298 K is based on the results of the relative rate studies of Tuazon *et al.*[1] and Sehested *et al.*,[2] which are in good agreement. Since studies have only been carried out at room temperature, no temperature dependence is recommended.

References

[1] E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, Int. J. Chem. Kinet. **24**, 639 (1992).

[2] J. Sehested, T. Ellermann, O. J. Nielsen, T. J. Wallington, and M. D. Hurley, Int. J. Chem. Kinet. **25**, 701 (1993).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CHFClCF_3$(HCFC-124) → $HCl + CFClCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.16\times10^{-12}\exp[-(1800\pm150)/T]$	276–376	Warren and Ravishankara, 1993[1]	(a)
$(2.62\pm0.50)\times10^{-15}$	298		
Relative Rate Coefficients			
$(2.7\pm0.6)\times10^{-15}$	298	Tuazon, Atkinson, and Corchnoy, 1992[2]	(b)
Reviews and Evaluations			
$1.1\times10^{-12}\exp(-1800/T)$	280–380	NASA, 1994[3]	(c)

Comments

(a) Cl atoms were generated by laser flash photolysis of CCl_4 at 222 nm. The pseudo-first-order decays of Cl atoms in excess HCFC were monitored by resonance fluorescence.

(b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Based on the results of Warren and Ravishankara[1] and Tuazon *et al.*[2]

Preferred Values

$k = 2.7\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.1\times10^{-12}\exp(-1800/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 276–376 K.

Reliability

$\Delta\log k = \pm0.1$ at 298 K.

$\Delta(E/R) = \pm500$ K.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported by Warren and Ravishankara[1] and Tuazon *et al.*,[2] which are in good agreement. The recommended temperature dependence is that reported by Warren and Ravishankara,[1] the only study carried out over a range of temperatures.

References

[1] R. F. Warren and A. R. Ravishankara, Int. J. Chem. Kinet. **25**, 833 (1993).
[2] E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, Int. J. Chem. Kinet. **24**, 639 (1992).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CHCl_2CF_3$(HCFC-123) → $HCl + CCl_2CF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.94\times10^{-12}\exp[-(1740\pm100)/T]$	276–382	Warren and Ravishankara, 1993[1]	(a)
$(1.15\pm0.30)\times10^{-14}$	298		
Relative Rate Coefficients			
$(1.22\pm0.18)\times10^{-14}$	295	Wallington and Hurley, 1992[2]	(b)
$(1.4\pm0.3)\times10^{-14}$	298	Tuazon, Atkinson, and Corchnoy, 1992[3]	(c)
Reviews and Evaluations			
$4.4\times10^{-12}\exp(-1750/T)$	298	NASA, 1994[4]	(d)

Comments

(a) Cl atoms were generated by laser flash photolysis of CCl_4 at 222 nm. The pseudo-first-order decays of Cl atoms in excess HCFC were monitored by resonance fluorescence.

(b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Based on the results of Warren and Ravishankara,[1] Wallington and Hurley,[2] and Tuazon *et al.*[3]

Preferred Values

$k = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.4 \times 10^{-12} \exp(-1750/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 276–382 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported in Refs. 1–3, which are in good agreement. The recommended temperature dependence is that reported by Warren and Ravishankara,[1] the only study carried out over a range of temperatures.

References

[1] R. F. Warren and A. R. Ravishankara, Int. J. Chem. Kinet. **25**, 833 (1993).

[2] T. J. Wallington and M. D. Hurley, Chem. Phys. Lett. **189**, 437 (1992).

[3] E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, Int. J. Chem. Kinet. **24**, 639 (1992).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + OCS \rightarrow SCl + CO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<1.1 \times 10^{-16}$	298	Eibling and Kaufman, 1983[1]	(a)
$<4 \times 10^{-15}$	298	Clyne *et al.*, 1984[2]	(b)
$<1 \times 10^{-14}$	298	Nava, Brobst, and Stief, 1985[3]	(c)
Reviews and Evaluations			
$<1.0 \times 10^{-16}$	298	NASA, 1994[4]	(d)

Comments

(a) Fast-flow discharge system with mass-spectrometric detection used. [Cl] monitored and from minimum observable change in [Cl] in presence of OCS upper limit to k obtained. SCl_2^+ was observed in small concentrations and if it is assumed to be due solely to the reaction of Cl with OCS, a lower limit of $k > 10^{-18}$ cm^3 molecule^{-1} s^{-1} can be derived.

(b) Discharge flow study of OCS removal in excess Cl. $[OCS^+]$ monitored by mass spectrometry. No consumption of OCS detectable, leading to upper limit to k.

(c) Flash photolysis of CCl_4 to produce Cl atoms in excess OCS. [Cl] monitored by resonance fluorescence. No consumption of Cl detected with OCS in range 100–300 Torr, leading to upper limit to k.

(d) Accepted upper limit obtained by Eibling and Kaufman.[1]

Preferred Values

$k < 1.0 \times 10^{-16}$ at 298 K.

Comments on Preferred Values

The reaction of Cl atoms with OCS is extremely slow and only upper limits to the rate coefficient have been obtained. The lowest of these[1] is preferred.

References

[1] R. E. Eibling and M. Kaufman, Atmos. Environ. **17**, 429 (1983).

[2] M. A. A. Clyne, A. J. MacRobert, T. P. Murrells, and L. J. Stief, J. Chem. Soc. Faraday Trans. 2, **80**, 877 (1984).

[3] D. F. Nava, W. D. Brobst, and L. J. Stief, J. Phys. Chem. **89**, 4703 (1985).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

$Cl + CS_2 + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<5\times10^{-15}$ (Air, 300 Torr)	293	Nicovich, Shackelford, and Wine, 1990[1]	(a)
Relative Rate Coefficients			
$(0.83\pm0.17)\times10^{-13}$ (Air, 760 Torr)	298	Martin, Barnes, and Becker, 1987[2]	(b)
$<4\times10^{-15}$ (Air, 700 Torr)	298	Wallington, Andino, and Potts, 1991[3]	(c)
Reviews and Evaluations			
$<4\times10^{-15}$	200–300	NASA, 1994[4]	(d)

Comments

(a) Pulsed laser photolysis of Cl_2 in CS_2, N_2, O_2 mixtures over the pressure range of 30–300 Torr and the temperature range of 193–258 K. [Cl] monitored by resonance fluorescence. Experiments in absence of O_2 reveal reversible adduct formation and establishment of equilibrium between Cl, CS_2, and CS_2Cl. Thermodynamic parameters for equilibrium derived. Upper limit tabulated for overall removal of CS_2 in presence of O_2 is for all channels of $CS_2Cl + O_2$ reaction which do not lead to Cl atom formation.

(b) Steady state photolysis of Cl_2 in presence of CS_2, N_2, O_2, and reference compound (CH_4 or CH_3Cl). [CS_2] and [CH_4] or [CH_3Cl] monitored by quadrupole mass spectrometry. Constant total pressure of 760 Torr. [N_2]/[O_2] varied. $k(Cl + CH_3Cl)=5.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} and $k(Cl + CH_4)=1.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} used.[5]

(c) Steady state photolysis of Cl_2 in the presence of CS_2, N_2, O_2, and the reference compound (CH_4, CH_3Cl, or CHF_2Cl). [CS_2] and concentration of reference compound monitored by FTIR. CH_4 and CH_3Cl shown to be unsuitable as reference compounds. Results suggest CHF_2Cl to be suitable. Value of $k(Cl + CHF_2Cl)/k(Cl + CH_4)<0.04$ measured in same study and combined with $k(Cl + CH_4)=1.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (Ref. 6) and measured $k(Cl+CS_2)/k(Cl + CHF_2Cl)$ in presence of O_2 to give tabulated upper limit to k.

(d) Accepted the value of Wallington *et al.*[3]

Preferred Values

$k\leq4\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K in air at 1 bar.

Comments on Preferred Values

The overall reaction of Cl with CS_2 appears to be too slow to be of importance in the atmosphere. Nicovich *et al.*[1] have shown that it proceeds initially by rapid formation of the $ClCS_2$ adduct, as suggested earlier by Martin *et al.*,[2] but the subsequent reaction of the adduct with O_2 appears to be slow.

The recommended upper limit is that of Wallington *et al.*[3] which agrees with the work of Nicovich *et al.*[1] Wallington *et al.*[3] have suggested that the value obtained by Martin *et al.*[2] was erroneously high due to complexities in their system arising from HO radical production from the reference compounds which were chosen.

References

[1] J. M. Nicovich, C. J. Shackelford, and P. H. Wine, J. Phys. Chem. **94**, 2896 (1990).
[2] D. Martin, I. Barnes, and K. H. Becker, Chem. Phys. Lett. **140**, 195 (1987).
[3] T. J. Wallington, J. M. Andino, and A. R. Potts, Chem. Phys. Lett. **176**, 103 (1991).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] NASA Evaluation No. 7, 1985 (see references in Introduction).
[6] NASA Evaluation No. 8, 1987 (see references in Introduction).

Cl + $CH_3SCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.8×10^{-10} (3 Torr N_2)	297	Stickel *et al.*, 1992[1]	(a)
$(3.3\pm0.5)\times10^{-10}$ (700 Torr N_2)	297		
Relative Rate Coefficients			
$(3.2\pm0.3)\times10^{-10}$ (740 Torr N_2)	295	Nielsen *et al.*, 1990[2]	(b)

Comments

(a) Rate coefficient measurements used pulsed laser photolysis of $COCl_2$-CH_3SCH_3-N_2 mixtures at 266 nm. [Cl] was monitored by resonance fluorescence. Some experiments were carried out with CD_3SCD_3 and $C_2H_5SC_2H_5$. Yield of HCl studied by 248 nm pulsed laser photolysis of $COCl_2$-CH_3SCH_3-CO_2-N_2 mixtures over the pressure range 0.6–203 Torr. [HCl] monitored by tunable diode laser spectroscopy. Reaction studied over the temperature range 240–421 K.

(b) Photolysis of mixtures of $COCl_2$-CH_3SCH_3-cyclohexane-N_2 in a Teflon chamber. [Cyclohexane] and [CH_3SCH_3] measured at intervals by GC. k(Cl + cyclohexane) = 3.1×10^{-10} cm^3 molecule^{-1} s^{-1} used.[3]

Preferred Values

$k=3.3\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar N_2.

Reliability

$\Delta\log k=\pm0.2$ at 298 K and 1 bar N_2.

Comments on Preferred Values

The most recent study of this reaction by Stickel *et al.*[1] shows the reaction kinetics to have a complex dependency on temperature and pressure. The overall reaction rate is close to collisional and increases with decreasing temperature and with increasing pressure. The HCl yield approaches unity as the pressure tends to zero but decreases to a value of ~0.5 at 203 Torr N_2 and 297 K.

These findings are interpreted in terms of the occurrence of two reaction channels, Cl abstraction and adduct formation. At low pressures the abstraction channel is dominant but with increasing pressure the adduct can be stabilized leading to an increase in the total k as pressure increases and temperature decreases.

Until the reaction is studied in more detail and a complete analysis of the temperature and pressure dependence can be made our recommendations are limited to high pressures and 298 K. They are based on the results of Stickel *et al.*[1] and Nielsen *et al.*[2] which are in excellent agreement. There is also a value of 2.0×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K and 760 Torr N_2 reported by Barnes *et al.*,[4] but no experimental details are given.

References

[1] R. E. Stickel, J. M. Nicovich, S. Wang, Z. Zhao, and P. H. Wine, J. Phys. Chem. **96**, 9875 (1992).

[2] O. J. Nielsen, H. W. Sidebottom, L. Nelson, O. Rattigan, J. Treacy, and D. J. O'Farrell, Int. J. Chem. Kinet. **22**, 603 (1990).

[3] R. Atkinson and S. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

[4] I. Barnes, V. Bastian, K. H. Becker, and D. Martin, *Biogenic Sulfur in the Environment,* edited by E. S. Saltzman and W. J. Cooper, ACS Symposium Series 393, p. 476 (1989).

$HO + Cl_2 \rightarrow HOCl + Cl$

$\Delta H° = 4.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.5\pm0.3)\times10^{-14}$	298	Leu and Lin, 1979[1]	(a)
7.4×10^{-14}	298	Ravishankara, Eisele, and Wine, 1983[2]	(a)
$(6.7\pm0.7)\times10^{-14}$	298	Loewenstein and Anderson, 1984[3]	(a)
$1.7\times10^{-12}\exp[-(911\pm373)/T]$	253–333	Boodaghians *et al.*, 1987[4]	(a)
$(6.8\pm1.0)\times10^{-14}$	293		
Reviews and Evaluations			
$1.4\times10^{-12}\exp(-900/T)$	250–330	NASA, 1994[5]	(b)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO.

(b) Based on the results of Leu and Lin,[1] Ravishankara *et al.*,[2] Loewenstein and Anderson,[3] and Boodaghians *et al.*[4]

Preferred Values

$k=6.7\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.4\times10^{-12}\exp(-900/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–330 K.

Reliability

$\Delta\log k=\pm0.1$ at 298 K.

$\Delta(E/R)=\pm400$ K.

Comments on Preferred Values

The preferred room temperature value is the average of the values reported by Leu and Lin,[1] Ravishankara *et al.*,[2] Loewenstein and Anderson,[3] and Boodaghians *et al.*[4] All of these studies were carried out in a discharge flow system with resonance fluorescence detection of HO radicals. The temperature dependence is from the study of Boodaghians *et al.*[4] Loewenstein and Anderson[3] determined that the exclusive products are Cl + HOCl.

References

[1] M. T. Leu and C. L. Lin, Geophys. Res. Lett. **6**, 425 (1979).
[2] A. R. Ravishankara, F. L. Eisele, and P. H. Wine, J. Chem. Phys. **78**, 1140 (1983).
[3] L. M. Loewenstein and J. G. Anderson, J. Phys. Chem. **88**, 6277 (1984).
[4] R. B. Boodaghians, I. W. Hall, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **83**, 529 (1987).
[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

$HO + HCl \rightarrow H_2O + Cl$

$\Delta H° = -67.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.8\pm0.3)\times10^{-13}$	298	Sharkey and Smith, 1993[1]	(a)
$(5.4\pm0.25)\times10^{-13}$	216		
$(5.6\pm0.45)\times10^{-13}$	178		
$(5.2\pm0.3)\times10^{-13}$	138		
Reviews and Evaluations			
$2.4\times10^{-12}\exp(-330/T)$	200–300	IUPAC, 1992[2]	(b)
$2.6\times10^{-12}\exp(-350/T)$	200–300	NASA, 1994[3]	(b)

Comments

(a) Pulsed laser photolysis of HNO_3 at 266 nm with LIF detection of HO radical decay in excess HCl.

(b) Based on the data of Molina *et al.*,[4] Keyser,[5] and Ravishankara *et al.*,[6] which gave higher room temperature values than earlier data.

Preferred Values

$k=8.1\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=2.4\times10^{-12}\exp(-330/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k=\pm0.1$ at 298 K.
$\Delta(E/R)=\pm150$ K.

Comments on Preferred Values

The recommendation is unchanged from our previous evaluation, IUPAC, 1992.[2] The studies of Molina *et al.*,[4] Keyser,[5] and Ravishankara *et al.*,[6] which paid careful attention to the [HCl] present in the experiments, all show room temperature values higher by about 20–25% than other studies.[7–14] Ravishankara *et al.*[6] showed that HCl losses can be a problem, leading to low *k* values, and this is a plausible cause of these discrepancies. The higher value, $k(298)=8.1\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (average of the 3 studies[4–6]) is the most reliable value. The preferred temperature-dependent expression for the range 200–300 K is obtained by weighted linear least squares fit to the data from these three studies.[4–6] Results of the recent low temperature study of Sharkey and Smith[1] are in good agreement with this recommendation down to 216 K but are significantly higher at 178 K and 138 K. Ravishankara *et al.*[6] reported the three parameter expression $k=4.5\times10^{-17}T^{1.65}\exp(112/T)$ cm^3 molecule^{-1} s^{-1} f the temperature range 240–1055 K.

References

[1] P. Sharkey and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **89**, 631 (1993).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] M. J. Molina, L. T. Molina, and C. A. Smith, Int. J. Chem. Kinet. **16**, 1151 (1984).
[5] L. Keyser, J. Phys. Chem. **88**, 4750 (1984).
[6] A. R. Ravishankara, P. H. Wine, J. R. Wells, and R. L. Thompson, Int. J. Chem. Kinet. **17**, 1281 (1985).
[7] B. D. Cannon, J. S. Robertshaw, I. W. M. Smith, and M. D. Williams, Chem. Phys. Lett. **105**, 380 (1984).
[8] D. Husain, J. M. C. Plane, and C. C. Xiang, J. Chem. Soc. Faraday Trans. 2, **80**, 713 (1984).
[9] G. A. Takacs and G. P. Glass, J. Phys. Chem. **77**, 1948 (1973).
[10] M. S. Zahniser, F. Kaufman, and J. G. Anderson, Chem. Phys. Lett. **27**, 507 (1974).
[11] I. W. M. Smith and R. Zellner, J. Chem. Soc. Faraday Trans. 2, **70**, 1045 (1974).
[12] A. R. Ravishankara, G. Smith, R. T. Watson, and D. D. Davis, J. Phys. Chem. **81**, 2220 (1977).
[13] W. Hack, G. Mex, and H.-Gg. Wagner, Ber. Bunsenges. Phys. Chem. **81**, 677 (1977).
[14] D. Husain, J. M. C. Plane, and N. K. H. Slater, J. Chem. Soc. Faraday Trans. 2, **77**, 1949 (1981).

$HO + HOCl \rightarrow ClO + H_2O$

$\Delta H°=-101.5$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=5.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=3.0\times10^{-12}\exp(-500/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k=\pm0.5$ at 298 K.
$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The only reported experimental value[1] has a large uncertainty. The preferred value is based on the midrange value of 5×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K from this study and an *A* factor of 3.0×10^{-12} cm^3 molecule^{-1} s^{-1}, i.e., equal to that for the HO + H_2O_2 reaction. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[2]

References

[1] C. A. Ennis and J. W. Birks, J. Phys. Chem. **92**, 1119 (1988).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + ClO \rightarrow HO_2 + Cl$ (1)
$\rightarrow HCl + O_2$ (2)

$\Delta H°(1)=-5.2$ kJ·mol^{-1}
$\Delta H°(2)=-233.2$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2$)

$k=1.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.1\times10^{-11}$ exp(120/T) cm^3 molecule^{-1} s^{-1} over the temperature range 200–373 K.

$k_1/k=0.98$ at 298 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm150$ K.

$\Delta(k_1/k)=^{+0.02}_{-0.12}$ at 298 K.

Comments on Preferred Values

The preferred rate coefficient k is based on the three studies[1–3] in which [ClO] was measured directly. The uncertainty reflects the differences in the 298 K values and the reported temperature coefficients. The measurement of the branching ratio for HCl formation based on measurement of the HCl stable product,[3] $k_1/k=0.98\pm0.12$, is more accurate since this is clearly the minor channel. However, the uncertainties do not allow the occurrence of this HCl channel to be eliminated completely. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] A. J. Hills and C. J. Howard, J. Chem. Phys. **81**, 4458 (1984).

[2] J. P. Burrows, T. J. Wallington, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **80**, 957 (1984).

[3] G. Poulet, G. Laverdet, and G. Le Bras, J. Phys. Chem. **90**, 159 (1986).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + OClO \rightarrow HOCl + O_2$ (1)
$\rightarrow HO_2 + ClO$ (2)

$\Delta H^\circ(1)=-213$ kJ·mol^{-1}

$\Delta H^\circ(2)=-18.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2$)

$k=7.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=4.5\times10^{-13}$ exp(800/T) cm^3 molecule^{-1} s^{-1} over the temperature range 290–480 K.

$k_2/k=0$.

Reliability

$\Delta\log k_1=\pm0.3$ at 298 K.

$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The preferred values are based on the single experimental study of Poulet *et al.*[1] in a discharge flow system with EPR and LIF detection of HO radical decay and molecular beam mass spectrometry detection of the product HOCl. Indication of curvature in the Arrhenius plot dictates caution in extrapolation beyond the experimental range. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[2]

References

[1] G. Poulet, H. Zagogianni, and G. Le Bras, Int. J. Chem. Kinet. **18**, 847 (1986).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + ClNO_2 \rightarrow HOCl + NO_2$

$\Delta H^\circ=-97$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.4×10^{-12} exp[$-(1250\pm155)/T$]	259–348	Ganske *et al.*, 1992[1]	(a)
$(3.6\pm0.2)\times10^{-14}$	298		
Reviews and Evaluations			
3.5×10^{-14}	298	IUPAC, 1992[2]	(b)
2.4×10^{-12} exp($-1250/T$)	260–350	NASA, 1994[3]	(c)

Comments

(a) Fast-flow discharge system. Pseudo-first-order decays of HO radicals in excess $ClNO_2$ were monitored by resonance fluorescence. Two different flow tube wall coatings, halocarbon wax and phosphoric acid, were used to check for possible heterogeneous reactions. Mass spectrometry showed HOCl to be the sole chlorine-containing product.

(b) Based on the room temperature results of Ganske *et al.*[4]

(c) Based on the results of Ganske *et al.*[1]

Preferred Values

$k=3.6\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=2.4\times10^{-12}\exp(-1250/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–350 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The preferred values are based on the results of the temperature-dependent study of Ganske *et al.*[1] Mass spectrometric studies showed HOCl to be the sole chlorine-containing product, with no evidence for production of $HONO_2$ or Cl_2, thereby showing that the only reaction pathway is that yielding $HOCl + NO_2$.

References

[1] J. A. Ganske, H. N. Berko, M. J. Ezell, and B. J. Finlayson-Pitts, J. Phys. Chem. **96**, 2568 (1992).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] J. A. Ganske, M. J. Ezell, H. N. Berko, and B. J. Finlayson-Pitts, Chem. Phys. Lett. **179**, 204 (1991).

$$\begin{aligned} HO + ClONO_2 &\rightarrow HOCl + NO_3 \quad (1)\\ &\rightarrow HO_2 + ClONO \quad (2)\\ &\rightarrow HONO_2 + ClO \quad (3)\end{aligned}$$

$\Delta H^\circ(1)=-66$ kJ·mol^{-1}
$\Delta H^\circ(2)=8.4$ kJ·mol^{-1}
$\Delta H^\circ(3)=-95.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2+k_3$)

$k=3.9\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.2\times10^{-12}\exp(-330/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 246–387 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The results of the only two reported studies of Ravishankara *et al.*[1] and Zahniser *et al.*[2] are in good agreement at 245 K (within 25%), considering the difficulties associated with handling $ClONO_2$. The preferred value is that of Zahniser *et al.*[2] Neither study reported any data on the reaction products. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] A. R. Ravishankara, D. D. Davis, G. Smith, G. Tesi, and J. Spencer, Geophys. Res. Lett. **4**, 7 (1977).

[2] M. S. Zahniser, J. S. Chang, and F. Kaufman, J. Chem. Phys. **67**, 997 (1977).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CH_3Cl \rightarrow H_2O + CH_2Cl$

$\Delta H^\circ = -77.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.90\times 10^{-14}\ T^{0.89}\exp[-(1447\pm 75)/T]$	295–955	Taylor *et al.*, 1993[1]	(a)
$(4.9\pm 0.6)\times 10^{-14}$	295		
Relative Rate Coefficients			
$3.78\times 10^{-18}\ T^2\exp[-(655\pm 74)/T]$	293–358	Hsu and DeMore, 1994[2]	(b)
3.53×10^{-14}	298		
Reviews and Evaluations			
$1.8\times 10^{-12}\exp(-1115/T)$	240–300	IUPAC, 1992[3]	(c)
$7.33\times 10^{-18}\ T^2\exp(-809/T)$	247–955	Atkinson, 1994[4]	(d)
$4.0\times 10^{-12}\exp(-1400/T)$	247–400	NASA, 1994[5]	(e)

Comments

(a) Laser photolysis system with LIF detection of HO radicals. Rate coefficients were measured at 742, 775, 875, 925, and 955 K, and combined with rate coefficients from a previous study[6] to obtain the cited temperature-dependent expression and 295 K rate coefficient.

(b) Relative rate method. HO radicals were generated by the UV photolysis of O_3 in the presence of water vapor. The concentrations of CH_3Cl and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3Cl)/k(HO + CH_3CHF_2) = (1.91\pm 0.45)\exp[-(195\pm 74)/T]$ is placed on an absolute base by using a rate coefficient of $k(HO + CH_3CHF_2) = 1.98\times 10^{-18}\ T^2\exp(-460/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Derived from the rate coefficient data of Howard and Evenson,[7] Perry *et al.*,[8] Davis *et al.*,[9] Paraskevopoulos *et al.*,[10] and Jeong and Kaufman.[11]

(d) Derived from the absolute rate coefficient data of Howard and Evenson,[7] Perry *et al.*,[8] Davis *et al.*,[9] Paraskevopoulos *et al.*,[10] Jeong and Kaufman,[11] and those listed by Taylor *et al.*,[1] using the three parameter equation $k = CT^2\exp(-D/T)$.

(e) Derived from the absolute rate coefficient data of Howard and Evenson,[7] Perry *et al.*,[8] Davis *et al.*,[9] Paraskevopoulos *et al.*,[10] Jeong and Kaufman,[11] and Taylor *et al.*[1,6] at temperatures <400 K and the relative rate coefficients of Hsu and DeMore.[2]

Preferred Values

$k = 4.2\times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.8\times 10^{-12}\exp(-1340/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

At room temperature and below, the absolute rate coefficients of Howard and Evenson,[7] Perry *et al.*,[8] Davis *et al.*,[9] Paraskevopoulos *et al.*,[10] Jeong and Kaufman,[11] and Taylor *et al.*[6] are in good agreement. The rate coefficients determined by Taylor *et al.*[6] at temperatures of ~428–485 K are significantly higher than those of Perry *et al.*[8] and Jeong and Kaufman,[11] and use of the rate data of Taylor *et al.*[1,6] leads to a rate expression which predicts rate coefficients at ~250 K which are 10–25% lower than those reported by Davis *et al.*[9] and Jeong and Kaufman.[11] The room temperature rate coefficient of Brown *et al.*[12] is ~20–25% higher than other absolute data,[6–11] and is not used in the evaluation. The rate coefficients of Howard and Evenson,[7] Perry *et al.*,[8] Davis *et al.*[9] Paraskevopoulos *et al.*,[10] Jeong and Kaufman,[11] and Taylor *et al.*[1] and those of Taylor *et al.*[6] as listed by Taylor *et al.*[1] (with the rate coefficients of Taylor *et al.*[6] being averaged at 473 and 475 K, 524 and 525 K, 667 K, and 695 K, and the rate coefficient at 735 K being omitted[1]) have been fitted to the three parameter equation $k = CT^2\exp(-D/T)$, resulting in $k = 7.33\times 10^{-18}\ T^2\times\exp(-809/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 247–955 K. The preferred Arrhenius expression, $k = A\times\exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = Ce^2\ T^2$ and $B = D + 2T$. The rate coefficients obtained from the relative rate study of Hsu and DeMore[2] are lower than the preferred values over the temperature range studied by Hsu and DeMore[2] (295–358 K), and the temperature-dependent expression of Hsu and DeMore[2] cited in the table leads to calculated rate coefficients at 240 K and 300 K which are 2% and 14% lower, respectively, than predicted from the three parameter equation.

References

[1] P. H. Taylor, Z. Jiang, and B. Dellinger, Int. J. Chem. Kinet. **25**, 9 (1993).

[2] K.-J. Hsu and W. B. DeMore, Geophys. Res. Lett. **21**, 805 (1994).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

[6] P. H. Taylor, J. A. D'Angelo, M. C. Martin, J. H. Kasner, and B. Dellinger, Int. J. Chem. Kinet. **21**, 829 (1989).

[7] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).

[8] R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. **64**, 1618 (1976).

[9] D. D. Davis, G. Machado, B. Conaway, Y. Oh, and R. Watson, J. Chem. Phys. **65**, 1268 (1976).

[10] G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, J. Phys. Chem. **85**, 561 (1981).

[11] K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).

[12] A. C. Brown, C. E. Canosa-Mas, and R. P. Wayne, Atmos. Environ. **24A**, 361 (1990).

$HO + CH_2FCl(HCFC\text{-}31) \rightarrow H_2O + CHFCl$

No new data have been published since our last evaluation.

Preferred Values

$k=4.4\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=2.0\times10^{-12}\exp(-1135/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k=\pm0.10$ at 298 K.

$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The rate coefficients measured by Howard and Evenson,[1] Watson *et al.*,[2] Handwerk and Zellner,[3] Paraskevopoulos *et al.*,[4] and Jeong and Kaufman[5] are in reasonably good agreement at temperatures $>\sim290$ K, although there is a significant discrepancy between the rate coefficients of Watson *et al.*[2] and Jeong and Kaufman[5] at ~250 K. The data from all five studies[1–5] have been fitted to the three parameter equation $k=CT^2\exp(-D/T)$, resulting in $k=3.77\times10^{-18}\,T^2\exp(-604/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 245–486 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A=Ce^2\,T^2$ and $B=D+2T$, and is identical to our previous evaluation, IUPAC, 1992.[6]

References

[1] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).

[2] R. T. Watson, G. Machado, B. Conaway, S. Wagner, and D. D. Davis, J. Phys. Chem. **81**, 256 (1977).

[3] V. Handwerk and R. Zellner, Ber. Bunsenges. Phys. Chem. **82**, 1161 (1978).

[4] G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, J. Phys. Chem. **85**, 561 (1981).

[5] K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).

[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CH_2Cl_2 \rightarrow H_2O + CHCl_2$

$\Delta H^\circ=-87.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.01\times10^{-15}\,T^{1.09}\exp[-(771\pm48)/T]$	295–955	Taylor *et al.*, 1993[1]	(a)
$(1.47\pm0.18)\times10^{-13}$	295		
Relative Rate Coefficients			
$1.92\times10^{-18}\,T^2\exp[-(166\pm29)/T]$	293–360	Hsu and DeMore, 1994[2]	(b)
9.34×10^{-14}	298		
$1.51\times10^{-18}\,T^2\exp[-(60\pm20)/T]$	298–368	Hsu and DeMore, 1994[2]	(b)
1.13×10^{-13}	298		
Reviews and Evaluations			
$4.4\times10^{-12}\exp(-1030/T)$	240–300	IUPAC, 1992[3]	(c)
$6.14\times10^{-18}\,T^2\exp(-389/T)$	245–955	Atkinson, 1994[4]	(d)
$3.8\times10^{-12}\exp(-1050/T)$	245–400	NASA, 1994[5]	(e)

Comments

(a) Laser photolysis system with LIF detection of HO radicals. These data supersede the earlier data from this group.[6]

(b) Relative rate method. HO radicals were generated by the UV photolysis of O_3 in the presence of water vapor. CH_2Cl_2 and CH_3CHF_2 (or CH_3CH_2F) concentrations were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(HO + CH_2Cl_2)/k(HO + CH_3CHF_2) = (0.97 \pm 0.09) \exp[(294 \pm 29)/T]$ and $k(HO + CH_2Cl_2)/k(HO + CH_3CH_2F) = (0.32 \pm 0.02) \exp[(171 \pm 20)/T]$ are placed on an absolute basis by using rate coefficients of $k(HO + CH_3CHF_2) = 1.98 \times 10^{-18}\ T^2 \exp(-460/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation) and $k(HO + CH_3CH_2F) = 4.72 \times 10^{-18}\ T^2 \exp(-213/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Derived from the absolute rate coefficients of Howard and Evenson,[7] Perry *et al.*,[8] Davis *et al.*,[9] and Jeong and Kaufman.[10]

(d) Derived from the absolute rate coefficient data of Howard and Evenson,[7] Perry *et al.*,[8] Davis *et al.*,[9] Jeong and Kaufman,[10] and Taylor *et al.*,[1] using the three parameter equation $k = CT^2 \exp(-D/T)$.

(e) Derived from the absolute rate coefficient data of Howard and Evenson,[7] Perry *et al.*,[8] Davis *et al.*,[9] Jeong and Kaufman,[10] and Taylor *et al.*,[1] using only the rate coefficients obtained at temperatures <400 K, and the relative rate coefficients of Hsu and DeMore.[2]

Preferred Values

$k = 1.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.7 \times 10^{-12} \exp(-920/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.20$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The relative rate coefficients of Hsu and DeMore[2] at 298 K are in reasonable agreement with the absolute rate coefficient of Davis *et al.*,[9] but are ~20–35% lower than the absolute rate coefficients of Howard and Evenson,[7] Perry *et al.*,[8] Jeong and Kaufman,[10] and Taylor *et al.*[1] A fit of the absolute rate coefficients of Howard and Evenson,[7] Perry *et al.*,[8] Davis *et al.*,[9] Jeong and Kaufman,[10] and Taylor *et al.*[1] to the three parameter equation $k = CT^2 \exp(-D/T)$ leads to $k = 6.14 \times 10^{-18}\ T^2 \exp(-389/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 245–955 K, with a 298 K rate coefficient of 1.48×10^{-13} cm^3 molecule^{-1} s^{-1}. The 298 K rate coefficients measured by Hsu and DeMore[2] relative to the reactions of the HO radical with CH_3CH_2F and CH_3CHF_2 are ~30% lower than this value obtained from the absolute rate data, and the value of C in the three parameter equation is lowered by 15% to $C = 5.2 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}, resulting in the three parameter equation $k = 5.2 \times 10^{-18}\ T^2 \times \exp(-390/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 245–955 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = Ce^2\ T^2$ and $B = D + 2T$. The uncertainty limits have been increased to take into account the discrepancies between the various studies.

References

[1] P. H. Taylor, Z. Jiang, and B. Dellinger, Int. J. Chem. Kinet. **25**, 9 (1993).
[2] K.-J. Hsu and W. B. DeMore, Geophys. Res. Lett. **21**, 805 (1994).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[5] NASA Evaluation No. 11, 1994 (see references in Introduction).
[6] P. H. Taylor, J. A. D'Angelo, M. C. Martin, J. H. Kasner, and B. Dellinger, Int. J. Chem. Kinet. **21**, 829 (1989).
[7] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[8] R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. **64**, 1618 (1976).
[9] D. D. Davis, G. Machado, B. C. Conaway, Y. Oh, and R. T. Watson, J. Chem. Phys. **65**, 1268 (1976).
[10] K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).

$HO + CHF_2Cl(HCFC\text{-}22) \rightarrow H_2O + CF_2Cl$

$\Delta H° = -76.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.1\times10^{-13}\exp[-(1516\pm53)/T]$	298–460	Orkin and Khamaganov, 1993[1]	(a)
$(4.9\pm0.45)\times10^{-15}$	298		
$1.74\times10^{-12}\exp[-(1701 \pm 39)/T]$	302–382	Yujing *et al.*, 1993[2]	(b)
5.99×10^{-15}	302		
Relative Rate Coefficients			
$2.32\times10^{-20}\ T^{2.58}\exp[-(740\pm45)/T]$	298–366	Hsu and DeMore, 1995[3]	(c)
4.69×10^{-15}	298		
Reviews and Evaluations			
$7.8\times10^{-13}\exp(-1530/T)$	240–300	IUPAC, 1992[4]	(d)
$1.51\times10^{-18}\ T^2\exp(-1000/T)$	250–482	Atkinson, 1989,[5] 1994[6]	(e)
$1.0\times10^{-12}\exp(-1600/T)$	250–400	NASA, 1994[7]	(f)

Comments

(a) Discharge flow system with EPR detection of HO radicals.

(b) Discharge flow system with resonance fluorescence detection of HO radicals.

(c) Relative rate method. HO radicals were generated by the UV photolysis of O_3 in the presence of water vapor. The concentrations of CHF_2Cl and CH_4 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CHF_2Cl)/k(HO + CH_4) = (0.24\pm0.03)\exp[(342\pm45)/T]$ is placed on an absolute basis by using a rate coefficient of $k(HO + CH_4) = 9.65\times10^{-20}\ T^{2.58}\exp(-1082/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Derived from the absolute rate coefficients of Atkinson *et al.*,[8] Howard and Evenson,[9] Watson *et al.*,[10] Chang and Kaufman,[11] Handwerk and Zellner,[12] Paraskevopoulos *et al.*,[13] and Jeong and Kaufman.[14]

(e) Derived from the absolute rate coefficients of Atkinson *et al.*,[8] Howard and Evenson,[9] Watson *et al.*,[10] Chang and Kaufman,[11] Handwerk and Zellner,[12] Paraskevoupolos *et al.*,[13] and Jeong and Kaufman,[14] using the three parameter equation $k = CT^2\exp(-D/T)$.

(f) Derived from the rate coefficients of Atkinson *et al.*,[8] Howard and Evenson,[9] Watson *et al.*,[10] Chang and Kaufman,[11] Handwerk and Zellner,[12] Paraskevopoulos *et al.*,[13] Jeong and Kaufman,[14] Orkin and Khamaganov,[1] and Hsu and DeMore.[3]

Preferred Values

$k=4.6\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=7.8\times10^{-13}\exp(-1530/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k = \pm0.10$ at 298 K.

$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

The absolute rate coefficients of Orkin and Khamaganov[1] and the relative rate coefficients of Hsu and DeMore[3] are in good agreement with previous absolute rate coefficients[8–14] and with our previous evaluation, IUPAC, 1992[4] (to within 12% of our previous evaluation[4] from 298–370 K and 21% at 460 K for the data of Orkin and Khamaganov[1] and to within 7% of our previous evaluation[4] for the data of Hsu and DeMore[3]). However, the absolute rate coefficients of Yujing *et al.*[2] are ~25% higher than our previous evaluation.[4] The absolute rate coefficients of Atkinson *et al.*,[8] Howard and Evenson,[9] Watson *et al.*,[10] Chang and Kaufman,[11] Handwerk and Zellner,[12] Paraskevopoulos *et al.*,[13] and Jeong and Kaufman[14] have been fitted to the three parameter equation $k=CT^2\exp(-D/T)$, resulting in $k=1.51\times10^{-18}\ T^2\exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–482 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = Ce^2\ T^2$ and $B=D+2T$. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 157 (1993).

[2] M. Yujing, Y. Wenxiang, P. Yuexiang, and Q. Lianxiong, J. Environ. Sci. **5**, 481 (1993).

[3] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

[5] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 1**, 1 (1989).

[6] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[7] NASA Evaluation No. 11, 1994 (see references in Introduction).

[8] R. Atkinson, D. A. Hansen, and J. N. Pitts, Jr., J. Chem. Phys. **63**, 1703 (1975).

[9] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[10] R. T. Watson, E. Machado, B. C. Conaway, S. Wagner, and D. D. Davis, J. Phys. Chem. **81**, 256 (1977).
[11] J. S. Chang and F. Kaufman, J. Chem. Phys. **66**, 4989 (1977).
[12] Handwerk and R. Zellner, Ber. Bunsenges Phys. Chem. **82**, 1161 (1978).
[13] G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, J. Phys. Chem. **85**, 561 (1981).
[14] K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).

$HO + CHFCl_2(HCFC\text{-}21) \rightarrow H_2O + CFCl_2$

$\Delta H^\circ = -85.3$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 3.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.8 \times 10^{-13} \exp(-1010/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Howard and Evenson,[1] Perry *et al.*,[2] Watson *et al.*,[3] Chang and Kaufman,[4] Paraskevopoulos *et al.*,[5] and Jeong and Kaufman[6] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.70 \times 10^{-18}\ T^2 \exp(-479/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 241–483 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = Ce^2\ T^2$ and $B = D + 2T$, and is identical to our previous evaluation, IUPAC, 1992.[7]

References

[1] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[2] R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. **64**, 1618 (1976).
[3] R. T. Watson, E. Machado, B. C. Conaway, S. Wagner, and D. D. Davis, J. Phys. Chem. **81**, 256 (1977).
[4] J. S. Chang and F. Kaufman, J. Chem. Phys. **66**, 4989 (1977).
[5] G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, J. Phys. Chem. **85**, 561 (1981).
[6] K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).
[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CHCl_3 \rightarrow H_2O + CCl_3$

$\Delta H^\circ = -106.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.65 \times 10^{-17}\ T^{1.52} \exp[-(261 \pm 42)/T]$	295–775	Taylor *et al.*, 1993[1]	(a)
$(1.12 \pm 0.10) \times 10^{-13}$	295		
Relative Rate Coefficients			
$1.03 \times 10^{-18}\ T^2 \exp[(35 \pm 64)/T]$	288–357	Hsu and DeMore, 1994[2]	(b)
9.37×10^{-14}	298		
Reviews and Evaluations			
$3.3 \times 10^{-12} \exp(-1030/T)$	240–300	IUPAC, 1992[3]	(c)
$1.80 \times 10^{-18}\ T^2 \exp(-129/T)$	245–775	Atkinson, 1994[4]	(d)
$2.0 \times 10^{-12} \exp(-900/T)$	245–400	NASA, 1994[5]	(e)

Comments

(a) Laser photolysis system with LIF detection of HO radicals. These data supersede previous measurements from this group.[6]

(b) Relative rate method. HO radicals were generated by the UV photolysis of O_3 in the presence of water vapor. The concentrations of $CHCl_3$ and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CHCl_3)/k(HO + CH_3CHF_2) = (0.52 \pm 0.11) \exp[(495 \pm 64)/T]$ is placed on an absolute basis by using a rate coefficient of $k(HO + CH_3CHF_2) = 1.98 \times 10^{-18}\ T^2 \exp(-460/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Derived using the absolute rate coefficients of Howard and Evenson,[7] Davis *et al.*,[8] and Jeong and Kaufman.[9]

(d) Derived using the absolute rate coefficient data of Howard and Evenson,[7] Davis *et al.*,[8] and Taylor *et al.*,[1] using the three parameter equation $k=CT^2 \exp(-D/T)$.

(e) Derived from the absolute rate coefficients of Howard and Evenson,[7] Davis *et al.*,[8] Jeong and Kaufman,[9] and Taylor *et al.*,[1] using only rate coefficients obtained at temperatures <400 K, and the relative rate coefficients of Hsu and DeMore.[2]

Preferred Values

$k=1.0\times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=9.3\times 10^{-13} \exp(-660/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Taylor *et al.*[1] (which supersede those of Taylor *et al.*[6]) at temperatures of 360–480 K are significantly lower than the rate coefficients of Jeong and Kaufman,[9] by up to a factor of ~1.7. The relative rate coefficients of Hsu and DeMore[2] are in good agreement with the absolute rate coefficient data[1,7–9] at 298 K, but have a lower temperature dependence than measured in the absolute rate studies.[1,7–9] The absolute rate coefficients of Howard and Evenson,[7] Davis *et al.*,[8] and Taylor *et al.*[1] have been fitted to the three parameter equation $k=CT^2 \exp(-D/T)$, resulting in $k=1.80\times 10^{-18}\ T^2 \exp(-129/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 245–775. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K, and is derived from the three parameter equation with $A = C\, e^2\, T^2$ and $B=D+2T$.

References

[1] P. H. Taylor, Z. Jiang, and B. Dellinger, Int. J. Chem. Kinet. **25**, 9 (1993).

[2] K.-J. Hsu and W. B. DeMore, Geophys. Res. Lett. **21**, 805 (1994).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 1**, 1 (1989).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

[6] P. H. Taylor, J. A. D'Angelo, M. C. Martin, J. H. Kasner, and B. Dellinger, Int. J. Chem. Kinet. **21**, 829 (1989).

[7] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).

[8] D. D. Davis, G. Machado, B. C. Conaway, Y. Oh, and R. T. Watson, J. Chem. Phys. **65**, 1268 (1976).

[9] K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).

$HO + CF_2Cl_2(CFC\text{-}12) \rightarrow HOCl + CF_2Cl$

$\Delta H° = 97$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k<7\times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k<1\times 10^{-12} \exp(-3540/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–478 K.

Comments on Preferred Values

The preferred values are based upon an estimated Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} and the upper limit to the rate coefficient determined at 478 K in the absolute rate study of Chang and Kaufman.[1] This yields $k<1\times 10^{-12} \exp(-3540/T)$ cm^3 molecule^{-1} s^{-1}, and is consistent with the lack of reaction observed by Cox *et al.*[2] in their relative rate study. The preferred values are identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] J. S. Chang and F. Kaufman, Geophys. Res. Lett. **4**, 192 (1977).

[2] R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, Atmos. Environ. **10**, 305 (1976).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CFCl_3(CFC\text{-}11) \rightarrow HOCl + CFCl_2$

$\Delta H° = 78.5$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k<5\times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k<1\times 10^{-12} \exp(-3650/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–480 K.

Comments on Preferred Values

The preferred values are based upon an estimated Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} and the upper limit to the rate coefficient determined at 480 K in the absolute rate study of Chang and Kaufman.[1] This yields $k<1\times10^{-12}\exp(-3650/T)$ cm^3 molecule^{-1} s^{-1}, and is consistent with the lack of reaction observed by Cox *et al.*[2] in their relative rate study. The preferred values are identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] J. S. Chang and F. Kaufman, Geophys. Res. Lett. **4**, 192 (1977).
[2] R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, Atmos. Environ. **10**, 305 (1976).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CCl_4 \rightarrow HOCl + CCl_3$

$\Delta H^\circ = 49.6$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k<5\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k<1\times10^{-12}\exp(-2260/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range ~250–300 K.

Comments on Preferred Values

The preferred upper limit to the 298 K rate coefficient is based on the relative rate study of Cox *et al.*,[1] with their upper limit to the rate coefficient being increased by a factor of 5. Assuming an Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1}, this leads to the upper limit to the Arrhenius expression given. The preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, Atmos. Environ. **10**, 305 (1976).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + C_2HCl_3 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=2.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=5.0\times10^{-13}\exp(445/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–420 K.

Reliability

$\Delta\log k = \pm0.10$ at 298
$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is derived from the mean of the values of Howard[1] and Chang and Kaufman.[2] The Arrhenius parameters are those of Chang and Kaufman,[2] with the *A*-factor reduced to yield the preferred value at 298 K. The room temperature rate coefficients reported by Kirchner,[3] Edney *et al.*,[4] Klöpffer *et al.*,[5] and Kirchner *et al.*,[6] which are not used in the derivation of the preferred values, are in general agreement with the preferred values, which are identical to our previous evaluation, IUPAC, 1992.[7]

References

[1] C. J. Howard, J. Chem. Phys. **65**, 4771 (1976).
[2] J. S. Chang and F. Kaufman, J. Chem. Phys. **66**, 4989 (1977).
[3] K. Kirchner, Chimia **37**, 1 (1983).
[4] E. O. Edney, T. E. Kleindienst, and E. W. Corse, Int. J. Chem. Kinet. **18**, 1355 (1986).
[5] W. Klöpffer, R. Frank, E.-G. Kohl, and F. Haag, Chemiker-Zeitung **110**, 57 (1986).
[6] K. Kirchner, D. Helf, P. Ott, and S. Vogt, Ber. Bunsenges. Phys. Chem. **94**, 77 (1990).
[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + C_2Cl_4 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=1.7\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=9.4\times10^{-12}\exp(-1200/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–420 K.

Reliability

$\Delta\log k=\pm0.10$ at 298 K.
$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The preferred 298 K value is derived from the mean of the values of Howard[1] and Chang and Kaufman.[2] The Arrhenius parameters are those of Chang and Kaufman.[2] The Arrhenius expression and 305 K rate coefficient reported by Kirchner,[3] and Kirchner *et al.*,[4] which are not used in the derivation of the preferred values, are in reasonable agreement with the preferred values, which are identical to our previous evaluation, IUPAC, 1992.[5]

References

[1] C. J. Howard, J. Chem. Phys. **65**, 4771 (1976).
[2] J. S. Chang and F. Kaufman, J. Chem. Phys. **66**, 4989 (1977).
[3] K. Kirchner, Chimia **37**, 1 (1983).
[4] K. Kirchner, D. Helf, P. Ott, and S. Vogt, Ber. Bunsenges. Phys. Chem. **94**, 77 (1990).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CH_3CF_2Cl$ (HCFC-142b) → $H_2O + CH_2CF_2Cl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.45\pm0.31)\times10^{-15}$	270	Zhang, Huie, and Kurylo, 1992[1]	(a)
Reviews and Evaluations			
$9.2\times10^{-13}\exp(-1705/T)$	240–300	IUPAC, 1992[2]	(b)
$1.77\times10^{-18}\,T^2\exp(-1174/T)$	223–427	Atkinson, 1994[3]	(c)
$1.3\times10^{-12}\exp(-1800/T)$	223–427	NASA, 1994[4]	(d)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO.
(b) Derived from the rate coefficient data of Howard and Evenson,[5] Watson *et al.*,[6] and Gierczak *et al.*[7]
(c) Derived from the absolute rate coefficient data of Howard and Evenson,[5] Watson *et al.*,[6] and Gierczak *et al.*,[7] using the three parameter equation $k=CT^2\times\exp(-D/T)$.
(d) Derived from the absolute rate coefficients of Howard and Evenson,[5] Watson *et al.*,[6] Handwerk and Zellner,[8] Paraskevopoulos *et al.*,[9] Liu *et al.*,[10] Gierczak *et al.*,[7] Zhang *et al.*,[1] and Zellner *et al.* (unpublished data, 1993).

Preferred Values

$k=3.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1}.
$k=9.2\times10^{-13}\exp(-1705/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k=\pm0.10$ at 298 K.
$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The rate coefficients obtained[1,5–12] exhibit a large degree of scatter, especially at temperatures $\lesssim300$ K. In particular, the rate coefficients measured by Clyne and Holt,[11] Brown *et al.*,[12] and, to a lesser extent, Handwerk and Zellner,[8] Paraskevopoulos *et al.*,[9] Liu *et al.*,[10] and Zhang *et al.*[1] are higher than those of Howard and Evenson,[5] Watson *et al.*,[6] and Gierczak *et al.*[7] Accordingly, the rate coefficient data of Howard and Evenson,[5] Watson *et al.*,[6] and Gierczak *et al.*[7] have been fitted to the three parameter equation $k=CT^2\times\exp(-D/T)$, resulting in $k=1.77\times10^{-18}\,T^2\exp(-1174/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 223–427 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A=C\,e^2\,T^2$ and $B=D+2T$, and is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] Z. Zhang, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. **96**, 1533 (1992).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 4303 (1976).
[6] R. T. Watson, G. Machado, B. Conaway, S. Wagner, and D. D. Davis, J. Phys. Chem. **81**, 256 (1977).
[7] T. Gierczak, R. Talukdar, G. L. Vaghjiani, E. R. Lovejoy, and A. R. Ravishankara, J. Geophys. Res. **96**, 5001 (1991).

[8] V. Handwerk and R. Zellner, Ber. Bunsenges. Phys. Chem. **82**, 1161 (1978).
[9] G. Paraskevopoulos, D. L. Singleton and R. S. Irwin, J. Phys. Chem. **85**, 561 (1981).
[10] R. Liu, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. **94**, 3247 (1990).
[11] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).
[12] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

$HO + CH_3CFCl_2(HCFC\text{-}141b) \rightarrow H_2O + CH_2CFCl_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.82\pm0.65)\times10^{-15}$	250	Zhang, Huie, and Kurylo, 1992[1]	(a)
$(2.01\pm0.90)\times10^{-15}$	250		
$(3.39\pm0.82)\times10^{-15}$	270		
$(4.80\pm1.46)\times10^{-15}$	297		
$2.4\times10^{-12}\exp[-(1790\pm100)/T]$	298–479	Lancar, Le Bras, and Poulet, 1993[2]	(b)
$(5.7\pm1.5)\times10^{-15}$	298		
Relative Rate Coefficients			
$4.73\times10^{-20}\,T^{2.58}\exp[-(893\pm105)/T]$	298-358	Huder and DeMore, 1993[3]	(c,d)
5.73×10^{-15}	298		
$1.78\times10^{-18}\,T^2\exp[-(984\pm28)/T]$	298–358	Huder and DeMore, 1993[3]	(c,e)
5.85×10^{-15}	298		
Reviews and Evaluations			
$7.0\times10^{-13}\exp(-1425/T)$	240–300	IUPAC, 1992[4]	(f)
$1.35\times10^{-18}\,T^2\exp(-893/T)$	233–393	Atkinson, 1994[5]	(g)
$1.7\times10^{-13}\exp(-1700/T)$	250–479	NASA, 1994[6]	(h)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO radicals. Experiments carried out with reduced flash energies or water vapor concentrations (resulting in lower initial HO radical concentrations) led to the lower measured rate coefficients cited in the table. These data supersede those of Liu *et al.*[7] at 243–298 K.

(b) Discharge flow system with EPR detection of HO radicals.

(c) Relative rate method. HO radicals were generated by the photolysis of H_2O-O_3 mixtures at 254 nm in H_2O-O_3-CH_3CFCl_2-CH_4 (or CH_3CCl_3)-Ar-O_2 mixtures. The concentrations of CH_3CFCl_2 and CH_4 (or CH_3CCl_3) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(HO + CH_3CFCl_2)/k(HO + CH_4) = (0.49\pm0.16)\times\exp[(189\pm105)/T]$ and $k(HO + CH_3CFCl_2/k(HO + CH_3CCl_3) = (0.79\pm0.07)\exp[-(74\pm28)/T]$ are placed on an absolute basis by use of rate coefficients of $k(HO + CH_4) = 9.65\times10^{-20}\,T^{2.58}\times\exp(-1082/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation) and $k(HO + CH_3CCl_3) = 2.25\times10^{-18}\,T^2\exp(-910/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Relative to $k(HO + CH_4)$.

(e) Relative to $k(HO + CH_3CCl_3)$.

(f) Based on the absolute rate coefficients of Talukdar *et al.*[8]

(g) Derived from the absolute rate coefficients of Talukdar *et al.*,[8] using the three parameter equation $k = CT^2\times\exp(-D/T)$.

(h) Derived from the rate coefficients of Liu *et al.*[7] (at temperatures $\geq$330 K), Talukdar *et al.*[8] (at temperatures $\geq$253 K), Zhang *et al.*,[1] Lancar *et al.*,[2] and Hsu and DeMore.[3]

Preferred Values

$k = 5.9\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.0\times10^{-13}\exp(-1425/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k = \pm0.15$ at 298 K.
$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

The absolute rate coefficients of Brown *et al.*[9] are higher than those from the absolute rate studies of Liu *et al.*,[7] Talukdar *et al.*,[8] Zhang *et al.*,[1] and Lancar *et al.*[2] at all temperatures studied,[9] and the rate coefficients of Liu *et al.*[7] at temperatures $\leq$298 K are significantly higher than those of Talukdar *et al.*,[8] Zhang *et al.*,[1] and Lancar *et al.*[2] The measurements of Zhang *et al.*[1] show that the earlier lower temperature ($\leqslant$298 K) data of Liu *et al.*[7] were in error due to the occurrence of secondary reactions of OH radicals with reaction products. The rate coefficients of Talukdar *et al.*,[8] Zhang *et al.*[1] (obtained at low flash energies and/or low water vapor concentrations and with high associated uncertainties), Lancar *et al.*,[2] and Huder and DeMore[3] are in good agreement, as are those of Talukdar *et al.*[8] and Liu *et al.*[7] at temperatures $\geqslant$330 K.

The rate coefficients of Talukdar *et al.*[8] have been fitted to the three parameter equation $k=CT^2 \exp(-D/T)$, resulting in $k=1.35\times10^{-18}\ T^2 \exp(-893/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 233–393 K. The preferred Arrhenius expression, $k=A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A=C\ e^2\ T^2$ and $B=D+2T$, and is identical to our previous evaluation, IUPAC, 1992.[4]

The rate coefficients of Huder and DeMore,[3] obtained relative to the reactions of the HO radical with CH_4 and CH_3CCl_3, are within 5% of those calculated from the preferred three parameter equation over the temperature range 298–358 K studied.[3]

References

[1] Z. Zhang, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. **96**, 1533 (1992).
[2] I. Lancar, G. Le Bras, and G. Poulet, J. Chim. Phys. **90**, 1897 (1993).
[3] K. Huder and W. B. DeMore, Geophys. Res. Lett. **20**, 1575 (1993).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).
[5] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[6] NASA Evaluation No. 11, 1994 (see references in Introduction).
[7] R. Liu, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. **94**, 3247 (1990).
[8] R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **95**, 5815 (1991).
[9] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

$HO + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.78\times10^{-18}\ T^{2.08} \exp[-(1068\pm108)/T]$	298–761	Jiang, Taylor, and Dellinger, 1992[1]	(a)
$(1.1\pm0.1)\times10^{-14}$	298		
$(1.2\pm0.2)\times10^{-14}$	298	Lancar, Le Bras, and Poulet, 1993[2]	(b)
Reviews and Evaluations			
$1.2\times10^{-12} \exp(-1440/T)$	240–300	IUPAC, 1992[3]	(c)
$2.25\times10^{-18}\ T^2 \exp(-910/T)$	243–379	Atkinson, 1994[4]	(d)
$1.8\times10^{-12} \exp(-1550/T)$	243–379	NASA, 1994[5]	(e)

Comments

(a) Laser photolysis system with LIF detection of HO radicals.

(b) Discharge flow system with EPR detection of HO radicals.

(c) Derived from the absolute rate coefficients of Finlayson-Pitts *et al.*[6] and the 243–379 K absolute rate coefficients of Talukdar *et al.*[7]

(d) Derived from the absolute rate coefficients of Finlayson-Pitts *et al.*[6] and the 243–379 K absolute rate coefficients of Talukdar *et al.*,[7] using the three parameter equation $k=CT^2 \exp(-D/T)$.

(e) The 298 K rate coefficient was derived from the absolute rate coefficients of Finlayson-Pitts *et al.*[6] and Talukdar *et al.*.[7] and the relative rate coefficient of DeMore.[8] The temperature dependence was that of Talukdar *et al.*[7]

Preferred Values

$k=9.5\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.2\times10^{-12} \exp(-1440/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k=\pm0.10$ at 298 K.

$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The absolute rate coefficients of Jiang *et al.*[1] and Lancar *et al.*[2] are somewhat higher than those of Finlayson-Pitts *et al.*[6] and Talukdar *et al.*,[7] with the discrepancy between the rate coefficients of Jiang *et al.*[1] and those of Finlayson-Pitts *et al.*[6] and Talukdar *et al.*[7] increasing with increasing temperature. A unit-weighted least-squares analysis of the absolute rate coefficients of Finlayson-Pitts *et al.*[6] and Talukdar *et al.*,[7] using the expression $k=CT^2 \exp(-D/T)$, leads to $k=2.25\times10^{-18}\ T^2 \exp(-910/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 243–379 K. The preferred Arrhenius expression, $k=A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A=C\ e^2\ T^2$ and $B=D+2T$. This recommendation is identical to our previous evaluation, IUPAC, 1992.[3]

The relative rate coefficients of DeMore,[8] when placed on an absolute basis by use of the present recommendation for the reaction of the HO radical with CH_4, lead to $k(HO + CH_3CCl_3)=4.92\times10^{-20}\ T^{2.58} \exp(-728/T)$ cm^3

molecule^{-1} s^{-1} over the temperature range 277–356 K, equivalent to an Arrhenius expression of $k=1.16\times10^{-12}$ $\times\exp(-1412/T)$ cm^3 molecule^{-1} s^{-1} centered at 265 K and a 298 K rate coefficient of 1.02×10^{-14} cm^3 molecule^{-1} s^{-1}, in excellent agreement with our recommendation.

References

[1] Z. Jiang, P. H. Taylor, and B. Dellinger, J. Phys. Chem. **96**, 8961 (1992).
[2] I. Lancar, G. Le Bras, and G. Poulet, J. Chim. Phys. **90**, 1897 (1993).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1, (1994).
[5] NASA Evaluation No. 11, 1994 (see references in Introduction).
[6] B. J. Finlayson-Pitts, M. J. Ezell, T. M. Jayaweera, H. N. Berko, and C. C. Lai, Geophys. Res. Lett. **19**, 1371 (1992).
[7] R. K. Talukdar, A. Mellouki, A.-M. Schmoltner, T. Watson, S. Montzka, and A. R. Ravishankara, Science **257**, 227 (1992).
[8] W. B. DeMore, Geophys. Res. Lett. **19**, 1367 (1992).

HO + CH_2ClCF_3(HCFC-133a) → H_2O + $CHClCF_3$

No new data have been published since our last evaluation.

Preferred Values

$k=1.3\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=5.2\times10^{-13}\exp(-1100/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–380 K.

Reliability
$\Delta\log k=\pm0.2$ at 298 K.
$\Delta(E/R)=\pm250$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of those of Howard and Evenson[1] and Handwerk and Zellner[2] (corrected to 298 K), and the temperature dependence is that obtained from a unit-weighted least-squares analysis of the data of Handwerk and Zellner.[2] The rate coefficients of Clyne and Holt[3] are in serious disagreement with those of Handwerk and Zellner,[2] and are not used in the evaluation. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[2] V. Handwerk and R. Zellner, Ber. Bunsenges. Phys. Chem. **82**, 1161 (1978).
[3] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + CH_2ClCF_2Cl(HCFC-132b) → H_2O + $CHClCF_2Cl$

No new data have been published since our last evaluation.

Preferred Values

$k=1.6\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=3.2\times10^{-12}\exp(-1580/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability
$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The corrected data of Watson *et al.*[1] are accepted, assuming that the observed C_2 haloalkene impurities present in the CH_2ClCF_2Cl sample react with the OH radical with a rate coefficient of 5×10^{-12} cm^3 molecule^{-1} s^{-1} independent of temperature. The rate coefficients of Jeong *et al.*[2] are higher, especially at <300 K, suggesting the presence of reactive impurities in the CH_2ClCF_2Cl sample used. The preferred values are identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, Int. J. Chem. Kinet. **11**, 187 (1979).
[2] K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. **88**, 1222 (1984).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + $CHFClCF_3$(HCFC-124) → H_2O + $CFClCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$3.38\times10^{-20}\ T^{2.58}\ \exp[-(715\pm40)/T]$	298–366	Hsu and DeMore, 1995[1]	(a,b)
7.38×10^{-15}	298		
$6.44\times10^{-13}\ \exp[-(1330\pm52)/T]$	298–356	Hsu and DeMore, 1995[1]	(a,c)
7.36×10^{-15}	298		
Reviews and Evaluations			
$5.4\times10^{-13}\ \exp(-1205/T)$	240–300	IUPAC, 1992[2]	(d)
$1.03\times10^{-18}\ T^2\ \exp(-675/T)$	210–425	Atkinson, 1994[3]	(e)
$8.0\times10^{-13}\ \exp(-1350/T)$	210–425	NASA, 1994[4]	(f)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or from O_3-H_2O mixtures in the UV, in H_2O (or H_2O-O_3)-$CHFClCF_3$-CH_4 (or CHF_2CHF_2)-O_2-N_2 mixtures. The concentrations of $CHFClCF_3$ and CH_4 (or CHF_2CHF_2) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(HO + CHFClCF_3)/k(HO + CH_4) = (0.35\pm0.04)\ \exp[(367\pm40)/T]$ and $k(HO + CHFClCF_3)/k(HO + CHF_2CHF_2) = (0.46\pm0.07) \times\exp[(300\pm52)/T]$ are placed on an absolute basis by using rate coefficients of $k(HO + CH_4) = 9.65\times10^{-20}\ T^{2.58}\ \exp(-1082/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation) and $k(HO + CHF_2CHF_2) = 1.4\times10^{-12} \times\exp(-1630/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Relative to $k(HO + CH_4)$.

(c) Relative to $k(HO + CHF_2CHF_2)$.

(d) Derived from the absolute rate coefficients of Watson *et al.*[5] and Gierczak *et al.*[6]

(e) Derived from the absolute rate coefficients of Watson *et al.*[5] and Gierczak *et al.*,[6] using the three parameter equation $k=CT^2\ \exp(-D/T)$.

(f) Derived from the absolute rate coefficients of Howard and Evenson,[7] Watson *et al.*,[5] and Gierczak *et al.*[6] and the relative rate coefficients of Hsu and DeMore.[1]

Preferred Values

$k = 9.5\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.4\times10^{-13}\ \exp(-1205/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k = \pm0.20$ at 298 K.

$\Delta(E/R) = \pm300$ K.

Comments on Preferred Values

At room temperature, the absolute and relative rate coefficients[1,5–7] range over a factor of ~1.7, with the absolute rate coefficient of Howard and Evenson[7] being the highest, and the relative rate coefficients of Hsu and DeMore[1] being the lowest. The rate coefficients of Watson *et al.*[5] and Gierczak *et al.*[6] are in excellent agreement, and the rate coefficients from these two studies[5,6] have been fitted to the three parameter equation $k=CT^2\ \exp(-D/T)$, resulting in $k = 1.03\times10^{-18}\ T^2\ \exp(-675/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210–425 K. The preferred Arrhenius expression, $k=A\ \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A=C\ e^2\ T^2$ and $B=D+2T$, and is identical to our previous evaluation, IUPAC, 1992.[2] The uncertainty limits have been increased to overlap the relative rate coefficient data of Hsu and DeMore.[1]

References

[1] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1994).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

[5] R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, Int. J. Chem. Kinet. **11**, 187 (1979).

[6] T. Gierczak, R. Talukdar, G. L. Vaghjiani, E. R. Lovejoy, and A. R. Ravishankara, J. Geophys. Res. **96**, 5001 (1991).

[7] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 4303 (1976).

$HO + CHCl_2CF_3(HCFC\text{-}123) \rightarrow H_2O + CCl_2CF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.1\times10^{-12}\exp[-(940\pm200)/T]$	295–385	Nielsen, 1991[1]	(a)
$(4.3\pm1.0)\times10^{-14}$	295		
Relative Rate Coefficients			
$5.54\times10^{-19}\,T^2\exp[-(95\pm36)/T]$	298–359	Hsu and DeMore, 1995[2]	(b)
3.45×10^{-14}	298		
Reviews and Evaluations			
$5.5\times10^{-13}\exp(-815/T)$	240–300	IUPAC, 1992[3]	(c)
$1.06\times10^{-18}\,T^2\exp(-283/T)$	213–400	Atkinson, 1994[4]	(d)
$7.0\times10^{-13}\exp(-900/T)$	213–400	NASA, 1994[5]	(e)

Comments

(a) Pulsed radiolysis system with resonance absorption detection of HO radicals.

(b) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or from O_3-H_2O mixtures in the UV, in H_2O (or H_2O-O_3)-$CHCl_2CF_3$-CH_3CHF_2-O_2-N_2 mixtures. The concentrations of $CHCl_2CF_3$ and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CHCl_2CF_3)/k(HO + CH_3CHF_2) = (0.28\pm0.03)\exp[(365\pm36)/T]$ is placed on an absolute basis by using a rate coefficient of $k(HO + CH_3CHF_2) = 1.98\times10^{-18}\,T^2\exp(-460/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Derived from the absolute rate coefficients of Howard and Evenson,[6] Watson *et al.*,[7] Liu *et al.*,[8] and Gierczak *et al.*[9]

(d) Derived from the absolute rate coefficients of Howard and Evenson,[6] Watson *et al.*,[7] Liu *et al.*,[8] and Gierczak *et al.*,[9] using the three parameter equation $k=CT^2\times\exp(-D/T)$.

(e) Derived from the rate coefficients of Howard and Evenson,[6] Watson *et al.*,[7] Liu *et al.*,[8] Gierczak *et al.*,[9] Nielsen,[1] Hsu and DeMore,[2] and Zellner *et al.* (unpublished data, 1993).

Preferred Values

$k=3.6\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=5.5\times10^{-13}\exp(-815/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k = \pm0.15$ at 298 K.

$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

The measured absolute rate coefficients of Howard and Evenson,[6] Watson *et al.*,[7] Liu *et al.*,[8] and Gierczak *et al.*[9] are in reasonable agreement, but are significantly lower than those of Brown *et al.*[10] and Nielsen.[1] The rate coefficients of Howard and Evenson,[6] Watson *et al.*,[7] Liu *et al.*,[8] and Gierczak *et al.*[9] have been fitted to the three parameter equation $k=CT^2\exp(-D/T)$, resulting in $k=1.06\times10^{-18}\,T^2\times\exp(-283/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 213–400 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A=C\,e^2\,T^2$ and $B=D+2T$, and is identical to our previous evaluation, IUPAC, 1992.[3]

The relative rate constants of Hsu and DeMore[2] are within 12% of those predicted from the recommended three parameter equation over the temperature range studied[2] (298–359 K).

References

[1] O. J. Nielsen, Chem. Phys. Lett. **187**, 286 (1991).
[2] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[5] NASA Evaluation No. 11, 1994 (see references in Introduction).
[6] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 4303 (1976).
[7] R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, Int. J. Chem. Kinet. **11**, 187 (1979).
[8] R. Liu, R. E. Huie and M. J. Kurylo, J. Phys. Chem. **94**, 3427 (1990).
[9] T. Gierczak, R. Talukdar, G. L. Vaghjiani, E. R. Lovejoy, and A. R. Ravishankara, J. Geophys. Res. **96**, 5001 (1991).
[10] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

HO + $CHFClCF_2Cl$(HCFC-123a) → H_2O + $CFClCF_2Cl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$9.2\times10^{-13}\exp[-(1281\pm85)/T]$	298–460	Orkin and Khamaganov, 1993[1]	(a)
$(1.23\pm0.10)\times10^{-14}$	298		

Comments

(a) Discharge flow system with EPR detection of HO radicals.

Preferred Values

$k=1.2\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=8.4\times10^{-13}\exp(-1255/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 298–460 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(E/R)=\pm400$ K.

Comments on Preferred Values

The preferred Arrhenius expression is obtained from a unit-weighted least-squares analysis of the absolute rate coefficients of Orkin and Khamaganov.[1]

References

[1] V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 157 (1993).

HO + $CHCl_2CF_2Cl$(HCFC-122) → H_2O + CCl_2CF_2Cl

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.13\times10^{-12}\exp[-(918\pm52)/T]$	298–460	Orkin and Khamaganov, 1993[1]	(a)
$(5.30\pm0.41)\times10^{-14}$	298		

Comments

(a) Discharge flow system with EPR detection of HO radicals.

Preferred Values

$k=5.1\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=1.2\times10^{-12}\exp(-940/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 298–460 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(E/R)=\pm400$ K.

Comments on Preferred Values

The preferred Arrhenius expression is obtained from a unit-weighted least-squares analysis of the absolute rate coefficients of Orkin and Khamaganov.[1]

References

[1] V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 157 (1993).

HO + CHFClCFCl$_2$ (HCFC-122a) → H$_2$O + CFClCFCl$_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$6.14\times10^{-18}\,T^2\exp[-(343\pm42)/T]$	294–362	Hsu and DeMore, 1995[1]	(a)
1.73×10^{-14}	298		

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or from the photolysis of O_3-H_2O mixtures in the UV, in H_2O (or H_2O-O_3)$CHFClCFCl_2$-CH_3CHF_2-O_2-N_2 mixtures. The concentrations of $CHFClCFCl_2$ and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + $CHFClCFCl_2$/k(HO + CH_3CHF_2) $=(0.31\pm0.04)\exp[(117\pm42)/T]$ is placed on an absolute basis by using a rate coefficient of k(HO + CH_3CHF_2) $=1.98\times10^{-18}\,T^2\exp(-460/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k=1.7\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=4.1\times10^{-12}\exp(-945/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

$\Delta(E/R)=\pm400$ K.

Comments on Preferred Values

The preferred values are based on the relative rate coefficients of Hsu and DeMore.[1] The preferred Arrhenius expression $k=A\exp(-B/T)$ is centered at 300 K and is derived from the cited three parameter expression, $k=CT^2\exp(-D/T)$, with $A=C\,e^2\,T^2$ and $B=D+2T$.

References

[1] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).

HO + CHCl$_2$CF$_2$CF$_3$(HCFC-225ca) → H$_2$O + CCl$_2$CF$_2$CF$_3$

No new data have been published since our last evaluation.

Preferred Values

$k=2.5\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.1\times10^{-12}\exp(-1130/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–400 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The rate coefficients measured by Zhang *et al.*[1] and Nelson *et al.*[2] over the temperature range 295–365 K are in good agreement within the experimental uncertainties. The rate coefficients measured by Brown *et al.*[3] at 251 K and 300 K are significantly higher, and are not used in the evaluation. The preferred 298 K rate coefficient is the average of those calculated from the Arrhenius expressions of Zhang *et al.*[1] and Nelson *et al.*,[2] and the preferred temperature dependence is the mean of those of Zhang *et al.*[1] and Nelson *et al.*[2] [a least-squares analysis of these data[1,2] yields $k=1.56\times10^{-12}\times\exp(-1239/T)$ cm^3 molecule^{-1} s^{-1}, largely weighted by the 270 K and 400 K rate coefficients of Zhang *et al.*[1]]. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] Z. Zhang, R. Liu, R. E. Huie, and M. J. Kurylo, Geophys. Res. Lett. **18**, 5 (1991).
[2] D. D. Nelson, Jr., M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. **96**, 249 (1992).
[3] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, K. Rothwell, and R. P. Wayne, Nature **347**, 541 (1990).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + $CHFClCF_2CF_2Cl$(HCFC-225cb) → H_2O+ $CFClCF_2CF_2Cl$

No new data have been published since our last evaluation.

Preferred Values

$k=8.9\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=5.5\times10^{-13}\exp(-1230/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–400 K.

Reliability

$\Delta\log k=\pm0.10$ at 298 K.

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The preferred values are derived from a least-squares analysis of the rate coefficients of Zhang *et al.*[1] and Nelson *et al.*,[2] which are in excellent agreement. The preferred values are identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] Z. Zhang, R. Liu, R. E. Huie, and M. J. Kurylo, Geophys. Res. Lett. **18**, 5 (1991).

[2] D. D. Nelson, Jr., M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. **96**, 249 (1992).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + $CH_3CF_2CFCl_2$ (HCFC-243cc)→ H_2O + $CH_2CF_2CFCl_2$

No new data have been published since our last evaluation.

Preferred Values

$k=2.4\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=7.0\times10^{-13}\exp(-1690/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–370 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The preferred values are based on the sole study of Nelson *et al.*,[1] and are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] D. D. Nelson, Jr., M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. **96**, 249 (1992).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + HC(O)Cl → H_2O + ClCO

No new data have been published since our last evaluation.

Preferred Values

$k<5\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the upper limit to the rate coefficient reported by Libuda *et al.*,[1] and is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] H. G. Libuda, F. Zabel, E. H. Fink, and K. H. Becker, J. Phys. Chem. **94**, 5860 (1990).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + $COCl_2$ → products

No new data have been published since our last evaluation.

Preferred Values

$k < 5\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit to the 298 K rate coefficient is based on the sole reported study of Nelson *et al.*,[1] with the preferred upper limit being increased by a factor of 5 over that cited by Nelson *et al.*,[1] and is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] L. Nelson, I. Shanahan, H. W. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 577 (1990).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CH_2ClCHO \rightarrow H_2O + CH_2ClCO$ (1)
$\rightarrow H_2O + CHClCHO$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(3.1\pm0.2)\times10^{-12}$	298±2	Scollard *et al.*, 1993[1]	(a)
Reviews and Evaluations			
3.0×10^{-12}	298	IUPAC, 1992[2]	(b)
3.1×10^{-12}	298	Atkinson, 1994[3]	(c)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO or C_2H_5ONO in CH_3ONO (or C_2H_5ONO)-NO-CH_2ClCHO-$CH_3C(O)CH_2CH_3$-air mixtures at atmospheric pressure. The concentrations of CH_2ClCHO and 2-butanone were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_2ClCHO)/k(HO + \text{2-butanone})$ is placed on an absolute basis by use of a rate coefficient of $k(HO + \text{2-butanone}) = 1.15\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[3]

(b) Based on the absolute rate coefficient of Balestra-Garcia *et al.*[4]

(c) Based on the rate coefficients of Balestra-Garcia *et al.*,[4] Starcke *et al.*,[5] and Scollard *et al.*[1]

Preferred Values

$k = 3.1\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.20$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of those of Balestra-Garcia *et al.*[4] and Scollard *et al.*,[1] which are in excellent agreement. The reaction is expected to proceed essentially totally by channel (1) at 298 K.

References

[1] D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, J. Phys. Chem. **97**, 4683 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[4] C. Balestra-Garcia, G. Le Bras and H. Mac Leod, J. Phys. Chem. **96**, 3312 (1992).

[5] J. Starcke, F. Zabel, L. Elsen, W. Nelsen, I. Barnes, and K. H. Becker, *Proceedings of the 5th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants* (Kluwer Academic, Dordrecht, The Netherlands, 1990), pp. 172–176.

HO + $CHFClCHO \rightarrow H_2O + CHFClCO$ (1)
$\rightarrow H_2O + CFClCHO$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.2\pm0.2)\times10^{-12}$	298±2	Scollard *et al.*, 1993[1]	(a)
Relative Rate Coefficients			
$(2.0\pm0.3)\times10^{-12}$	298±2	Scollard *et al.*, 1993[1]	(b)

Comments

(a) Laser photolysis system with resonance fluorescence detection of HO radicals.

(b) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO or C_2H_5ONO in CH_3ONO (or C_2H_5ONO)-CHFClCHO-toluene-air mixtures. The concentrations of CHFClCHO and toluene were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of k(HO + CHFClCHO)/k(HO + toluene) is placed on an absolute basis by using a rate coefficient of k(HO + toluene)$=5.96\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[2]

Preferred Values

$k=2.1\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.20$ at 298 K.

Comments on Preferred Values

The preferred value is an average of the absolute and relative rate coefficients of Scollard *et al.*,[1] which are in good agreement. The reaction is expected to proceed by channel (1) at room temperature.[1]

References

[1] D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, J. Phys. Chem. **97**, 4683 (1993).

[2] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

HO + $CHCl_2CHO \rightarrow H_2O + CHCl_2CO$ (1)
$\rightarrow H_2O + CCl_2CHO$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(2.3\pm0.1)\times10^{-12}$	298±2	Scollard *et al.*, 1993[1]	(a)
Reviews and Evaluations			
2.4×10^{-12}	298	IUPAC, 1992[2]	(b)
2.5×10^{-12}	298	Atkinson, 1994[3]	(c)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO or C_2H_5ONO in CH_3ONO (or C_2H_5ONO)-NO-$CHCl_2CHO$-$CH_3C(O)CH_2CH_3$-air mixtures at atmospheric pressure. The concentrations of $CHCl_2CHO$ and 2-butanone were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of k(HO + $CHCl_2CHO$)/k(HO + 2-butanone) is placed on an absolute basis by use of a rate coefficient of k(HO + 2-butanone)$=1.15\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[3]

(b) Based on the absolute rate coefficient of Balestra-Garcia *et al.*[4]

(c) Based on the rate coefficients of Balestra-Garcia *et al.*,[4] Starcke *et al.*,[5] and Scollard *et al.*[1]

Preferred Values

$k=2.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.20$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of those of Balestra-Garcia *et al.*[4] and Scollard *et al.*,[1] which are in excellent agreement. The reaction is expected to proceed essentially totally by channel (1) at 298 K.[1]

References

[1] D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, J. Phys. Chem. **97**, 4683 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2,** 1 (1994).

[4] C. Balestra-Garcia, G. Le Bras and H. Mac Leod, J. Phys. Chem. **96,** 3312 (1992).

[5] J. Starcke, F. Zabel, L. Elsen, W. Nelsen, I. Barnes, and K. H. Becker, *Proceedings of the 5th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants* (Kluwer Academic, Dordrecht, The Netherlands, 1990), pp. 172–176.

$HO + CF_2ClCHO \rightarrow H_2O + CF_2ClCO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.5\pm0.5)\times10^{-13}$	298±2	Scollard *et al.*, 1993[1]	(a)
Relative Rate Coefficients			
$(7.0\pm0.5)\times10^{-13}$	298±2	Scollard *et al.*, 1993[1]	(b)

Comments

(a) Laser photolysis system with resonance fluorescence detection of HO radicals.

(b) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO or C_2H_5ONO in CH_3ONO (or C_2H_5ONO)-CF_2ClCHO-ethanol-air mixtures. The concentrations of CF_2ClCHO and ethanol were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CF_2ClCHO)/k(HO + \text{ethanol})$ is placed on an absolute basis by using a rate coefficient of $k(HO + \text{ethanol})=3.27\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[2]

Preferred Values

$k=8.2\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.25$ at 298 K.

Comments on Preferred Values

The preferred value is an average of the absolute and relative rate coefficients of Scollard *et al.*,[1] which are in reasonable agreement.

References

[1] D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, J. Phys. Chem. **97**, 4683 (1993).

[2] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2,** 1 (1994).

$HO + CFCl_2CHO \rightarrow H_2O + CFCl_2CO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.3\pm0.1)\times10^{-12}$	298±2	Scollard *et al.*, 1993[1]	(a)
Relative Rate Coefficients			
$(1.1\pm0.2)\times10^{-12}$	298±2	Scollard *et al.*, 1993[1]	(b)

Comments

(a) Laser photolysis system with resonance fluorescence detection of HO radicals.

(b) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO or C_2H_5ONO in CH_3ONO (or C_2H_5ONO)-$CFCl_2CHO$-toluene-air mixtures. The concentrations of $CFCl_2CHO$ and toluene were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CFCl_2CHO)/k(HO + toluene)$ is placed on an absolute basis by using a rate coefficient of $k(HO + toluene) = 5.96 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.[2]

Preferred Values

$k = 1.2 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.20$ at 298 K.

Comments on Preferred Values

The preferred value is an average of the absolute and relative rate coefficients of Scollard *et al.*,[1] which are in good agreement.

References

[1] D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, J. Phys. Chem. **97**, 4683 (1993).

[2] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

$HO + CCl_3CHO \rightarrow H_2O + CCl_3CO$

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.28 \pm 0.25) \times 10^{-12}$	298±2	Barry *et al.*, 1994[1]	(a)
$(8.9 \pm 1.5) \times 10^{-13}$	298±2	Barry *et al.*, 1994[1]	(b)
Relative Rate Coefficients			
$(1.6 \pm 0.2) \times 10^{-12}$	298±2	Scollard *et al.*, 1993[2]	(c)
$(1.05 \pm 0.18) \times 10^{-12}$	298±2	Barry *et al.*, 1994[1]	(d)
Reviews and Evaluations			
1.4×10^{-12}	298	IUPAC, 1992[3]	(e)
1.3×10^{-12}	298	Atkinson, 1994[4]	(f)
$8.2 \times 10^{-12} \exp(-600/T)$	298-520	NASA, 1994[5]	(g)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO radicals.

(b) Discharge flow system with EPR detection of HO radicals.

(c) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO or C_2H_5ONO in CH_3ONO (or C_2H_5ONO)-CCl_3CHO-toluene-air mixtures. The concentrations of CCl_3CHO and toluene were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CCl_3CHO)/k(HO + toluene)$ is placed on an absolute basis by using a rate coefficient of $k(HO + toluene) = 5.96 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.[4]

(d) Relative rate method. HO radicals were generated by the photolysis of O_3 in the presence of water vapor in O_3-H_2O-CCl_3CHO-2-methylpropane-air mixtures at atmospheric pressure. The concentrations of CCl_3CHO and 2-methylpropane were measured by GC. The measuredrate coefficient ratio $k(HO + CCl_3CHO)/k(HO + 2\text{-methylpropane}) = 0.45 \pm 0.01$ is placed on an absolute basis by using a rate coefficient of $k(HO + 2\text{-methylpropane}) = 2.33 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.[4]

(e) Based on the room temperature rate coefficients of Dóbé *et al.*,[6] Nelson *et al.*,[7] and Balestra-Garcia *et al.*[8]

(f) Based on the room temperature rate coefficients of Starcke *et al.*,[9] Nelson *et al.*,[7] Balestra-Garcia *et al.*,[8] and Scollard *et al.*[2]

(g) The 298 K rate coefficient was the average of the three determinations of Barry *et al.*[1] The temperature dependence was that of Dóbé *et al.*[6]

Preferred Values

$k = 1.1 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

The most recent absolute and relative rate study of Barry *et al.*[1] supersedes previous measurements of Nelson *et al.*,[7] Balestra-Garcia *et al.*,[8] and Scollard *et al.*[2] The average of the three independent determinations of the rate coefficient by Barry *et al.*,[1] [$k=(1.1\pm0.2)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}], is ~30 lower than the absolute 298 K rate coefficient of Dóbé *et al.*,[6] but is in agreement with the value of Starcke *et al.*[9]

The preferred 298 K rate coefficient is the average value reported by Barry *et al.*[1] No temperature dependence is recommended.

References

[1] J. Barry, D. J. Scollard, J. J. Treacy, H. W. Sidebottom, G. Le Bras, G. Poulet, S. Téton, A. Chichinin, C. E. Canosa-Mas, D. J. Kinnison, R. P. Wayne, and O. J. Nielsen, Chem. Phys. Lett. **221**, 353 (1994).

[2] D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, J. Phys. Chem. **97**, 4683 (1993).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

[6] S. Dóbé, L. A. Khachatryan, and T. Bérces, Ber. Bunsenges. Phys. Chem. **93**, 847 (1989).

[7] L. Nelson, I. Shanahan, H. W. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 577 (1990).

[8] C. Balestra-Garcia, G. Le Bras, and H. Mac Leod, J. Phys. Chem. **96**, 3312 (1992).

[9] J. Starcke, F. Zabel, L. Elsen, W. Nelsen, I. Barnes, and K. H. Becker, *Proceedings of the 5th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants* (Kluwer Academic, Dordrecht, The Netherlands, 1990), pp. 172–176.

HO + $CH_3COCl \rightarrow H_2O + CH_2COCl$

No new data have been published since our last evaluation.

Preferred Values

$k=9\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm1.0$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the relative rate coefficient study of Nelson *et al.*[1] and is identical to our previous evaluation, IUPAC, 1992.[2] However, the data presented in Figure 5 of Nelson *et al.*[1] and in the earlier presentation of Nelson *et al.*[3] yields a rate coefficient for the reaction of HO radicals with $CH_3C(O)Cl$ of $k=6.8\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298±3 K, a factor of ~7.5 higher than cited in Nelson *et al.*[1] This apparent discrepancy requires clarification.

References

[1] L. Nelson, I. Shanahan, H. W. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 577 (1990).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] L. Nelson, J. J. Treacy, and H. W. Sidebottom, *Proceedings of the 3rd European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants, 1984* (Riedel, Dordrecht, Holland, 1984), pp. 258–263.

HO + $CHF_2OCHClCF_3 \rightarrow H_2O + CHF_2OCClCF_3$ (1)
$\rightarrow H_2O + CF_2OCHClCF_3$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$<3\times10^{-13}$	300±3	McLoughlin, Kane, and Shanahan, 1993[1]	(a)
Reviews and Evaluations			
2.1×10^{-14}	298	IUPAC, 1992[2]	(b)

Comments

(a) Relative rate method. HO radicals generated by the photolysis of CH_3ONO-NO-$CHF_2OCHClCF_3$-diethyl ether-air mixtures at atmospheric pressure. The concentrations of $CHF_2OCHClCF_3$ and diethyl ether were measured by GC. The upper limit to the rate coefficient ratio of $k(HO + CHF_2OCHClCF_3)/k(HO$ + diethyl ether) is placed on an absolute basis using a rate coefficient of k(HO + diethyl ether)$=1.31\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[3]

(b) Based on the absolute rate coefficient of Brown *et al.*[4]

Preferred Values

$k=2.1\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.5$.

Comments on Preferred Values

The preferred value is based on the absolute rate coefficient of Brown *et al.*,[4] with expanded uncertainty limits, and is identical to our previous evaluation, IUPAC, 1992.[2] The upper limit to the rate coefficient measured by McLoughlin *et al.*[1] is consistent with the preferred value.

References

[1] P. McLoughlin, R. Kane, and I. Shanahan, Int. J. Chem. Kinet. **25**, 137 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[4] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

$HO + CHF_2OCF_2CHFCl \rightarrow H_2O + CHF_2OCF_2CFCl$ (1)
$\rightarrow H_2O + CF_2OCF_2CHFCl$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$<3\times10^{-13}$	300±3	McLoughlin, Kane, and Shanahan, 1993[1]	(a)
Reviews and Evaluations			
$6.1\times10^{-13}\exp(-1080/T)$	300–430	IUPAC, 1992[2]	(b)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO-NO-CHF_2OCF_2CHFCl-diethyl ether-air mixtures at atmospheric pressure. The concentrations of CHF_2OCF_2CHFCl and diethyl ether were measured by GC. The measured upper limit to the rate coefficient ratio $k(HO + CHF_2OCF_2CHFCl)/k(HO$ + diethyl ether) is placed on an absolute basis by using a rate coefficient of k(HO + diethyl ether)$=1.31\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[3]

(b) Based on the absolute rate coefficients of Brown *et al.*[4]

Preferred Values

$k=1.6\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$k=6.1\times10^{-13}\exp(-1080/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 300–430 K.

Reliability

$\Delta\log k=\pm0.5$.

$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The preferred values are based on the absolute rate study of Brown *et al.*,[4] and are identical to our previous evaluation, IUPAC, 1992.[2] The upper limit to the rate coefficient measured by McLoughlin *et al.*[1] is consistent with the preferred values.

References

[1] P. McLoughlin, R. Kane and I. Shanahan, Int. J. Chem. Kinet. **25**, 137 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[4] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

$HO_2 + CF_3CCl_2O_2 \rightarrow O_2 + CF_3CCl_2O_2H$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.9 \pm 0.7) \times 10^{-12}$	298	Hayman *et al.*, 1994[1]	(a)

Comments

(a) Laser flash photolysis-UV absorption study of CF_3CCl_3-CH_3OH-O_2-N_2 mixtures. The kinetic data were obtained by analyzing two sets of transient decays for $CF_3CCl_2O_2$ and HO_2 radicals on the basis of a mechanism consisting of 10 reactions.

Preferred Values

$k = 1.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

While the above value of the rate coefficient seems reasonable, it has been derived from the analysis of a complex chemical system and requires independent verification to reduce the recommended error limits. It is interesting to note, by comparison with data for analogous halogenated RO_2 radicals, that while the α-substitution of Cl appears to reduce the rate coefficient slightly, the presence of the CF_3 group causes a much larger reduction in the value of k.

References

[1] G. D. Hayman, M. E. Jenkin, T. P. Murrells, and C. E. Johnson, Atmos. Environ. **28A**, 421 (1994).

$HO_2 + CH_2ClO_2 \rightarrow O_2 + CH_2ClO_2H$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.26 \times 10^{-13} \exp[(822 \pm 63)/T]$	251–600	Catoire *et al.*, 1994[1]	(a)
$(4.9 \pm 0.6) \times 10^{-12}$	298		

Comments

(a) Flash photolysis-UV absorption study of Cl_2-CH_3Cl-CH_3OH-O_2-N_2 mixtures at a total pressure of 760 Torr. Kinetic data were obtained by analyzing pairs of decay curves for CH_2ClO_2 and HO_2 radicals.

Preferred Values

$k = 5.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.2 \times 10^{-13} \exp(820/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–600 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The data of Catoire *et al.*[1] indicate that the rate coefficients of the reactions of CH_2ClO_2 and CH_3O_2 radicals with the HO_2 radical at 298 K are similar, as are their temperature dependences. This is in marked contrast to the self reactions of CH_2ClO_2 and CH_3O_2 radicals where chlorine substitution greatly enhances the rate coefficient. Confirmation of the above data is required.

The products of the reaction are not well characterized. The results[2,3] from the Cl atom-initiated photo-oxidation of CH_3Cl indicate the possible formation of the hydroperoxide, CH_2ClOOH. At the same time the observation in these earlier steady-state experiments[2,3] of an excess of H_2O over H_2O_2 formation has given rise to the suggestion of an alternative pathway, $HO_2 + CH_2ClO_2 \rightarrow H_2O + O_2 + HCOCl$. More information from product studies is needed.

References

[1] V. Catoire, R. Lesclaux, P. D. Lightfoot, and M.-T. Rayez, J. Phys. Chem. **98**, 2899 (1994).
[2] E. Sanhueza and J. Heicklen, J. Phys. Chem. **79**, 7 (1975).
[3] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **12**, 1001 (1980).

$NO_3 + HCl \rightarrow HNO_3 + Cl$

$\Delta H^\circ = 4.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<7\times10^{-18}$	298	Cantrell *et al.*, 1987[1]	(a)
$<5\times10^{-17}$	298	Mellouki *et al.*, 1989[2]	(b)
$<2.4\times10^{-17}$	298	Canosa-Mas *et al.*, 1989[3]	(c)
Reviews and Evaluations			
$<5\times10^{-17}$	298	NASA, 1994[4]	(d)

Comments

(a) Value derived from computer fits of time-concentration data for reactants and products monitored by FTIR absorption spectrometry.

(b) Discharge flow-EPR technique. Value derived from fitting to a complex mechanism.

(c) Discharge flow-multipath absorption technique. No reaction observed at room temperature. At higher temperatures (333–473 K), values derived from fitting to a complex mechanism yielded the Arrhenius expression of $k = 4\times10^{-12}\exp(-3330/T)$ cm^3 molecule^{-1} s^{-1}.

(d) Based on the results of Mellouki *et al.*[2]

Preferred Values

$k<5\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is the upper limit to the rate coefficient reported by Mellouki *et al.*[2] in a study using the discharge flow-EPR technique. Somewhat lower upper limits have been reported by Cantrell *et al.*[1] and by Canosa-Mas *et al.*[3] Canosa-Mas *et al.*[3] also reported Arrhenius parameters at higher temperatures (over the range 333–473 K). The preferred value indicates that this reaction is not important in the chemistry of the atmosphere.

References

[1] C. A. Cantrell, J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert, J. Phys. Chem. **91**, 6017 (1987).

[2] A. Mellouki, G. Poulet, G. Le Bras, R. Singer, J. P. Burrows, and G. K. Moortgat, J. Phys. Chem. **93**, 8017 (1989).

[3] C. E. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **85**, 709 (1989).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

$NO_3 + C_2HCl_3 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k=2.9\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.3$ at 298 K.

Comments on Preferred Values

The preferred value is derived from the relative rate coefficients measured by Atkinson *et al.*,[1] and is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] R. Atkinson, S. M. Aschmann, and M. A. Goodman, Int. J. Chem. Kinet. **19**, 299 (1987).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$NO_3 + C_2Cl_4 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k < 1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is derived from the relative rate coefficients measured by Atkinson *et al.*,[1] and is identical to our previous evaluation, IUPAC, 1992.[2] The upper limit to the rate coefficient has been increased over that derived from the relative rate coefficient data.[1]

References

[1] R. Atkinson, S. M. Aschmann, and M. A. Goodman, Int. J. Chem. Kinet. **19**, 299 (1987).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$ClO + HO_2 \rightarrow HOCl + O_2$ (1)
$\rightarrow HCl + O_3$ (2)

$\Delta H°(1) = -194$ kJ·mol^{-1}
$\Delta H°(2) = -66$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 5.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.6 \times 10^{-13} \exp(710/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.
$k_2/k < 0.003$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The data of Cattell and Cox[1] are in good agreement with the earlier measurements,[2–5] and the absence of a pressure dependence excludes a possible addition channel. The lowest upper limit for HCl formation via channel (2) is $k_2 \leq 1.5 \times 10^{-14}$ cm^3 s^{-1} at 298 K.[5] The preferred value at room temperature is based on the results reported in Refs. 1–5, and the recommended temperature dependence is from Ref. 3. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[6]

References

[1] F. C. Cattell and R. A. Cox, J. Chem. Soc. Faraday Trans. 2, **82**, 1413 (1986).
[2] B. Reimann and F. Kaufman, J. Chem. Phys. **69**, 2925 (1978).
[3] R. M. Stimpfle, R. A. Perry, and C. J. Howard, J. Chem. Phys. **71**, 5183 (1979).
[4] T. J. Leck, J. E. Cook, and J. W. Birks, J. Chem. Phys. **72**, 2364 (1980).
[5] J. P. Burrows and R. A. Cox, J. Chem. Soc. Faraday Trans. 1, **77**, 2465 (1981).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$ClO + O_3 \rightarrow ClOO + O_2$ (1)
$\rightarrow OClO + O_2$ (2)

$\Delta H°(1) = -146.8$ kJ·mol^{-1}
$\Delta H°(2) = -148.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k_1 < 1.5 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 < 1 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit for k_1 is based on the results of the study of Stevens and Anderson.[1] The preferred upper limit for k_2 is based on the data of DeMore *et al.*[2] and Wongdontri-Stuper *et al.*[3] These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4] The upper limit of Stevens and Anderson[1] at room temperature can be combined with their measured rate coefficient at 413 K to derive $A = 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $E/R > 3600$ K. For k_2 one can estimate $A = 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and derive $E/R > 4000$ K.

References

[1] P. S. Stevens and J. G. Anderson, Geophys. Res. Lett. **17**, 1287 (1990).
[2] W. B. DeMore, C. L. Lin, and S. Jaffe, presented at ACS National Meeting, Philadelphia, PA, 1975.
[3] W. Wongdontri-Stuper, R. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **10**, 163 (1979).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$ClO + NO \rightarrow Cl + NO_2$

$\Delta H° = -37.4$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=1.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=6.2\times10^{-12}$ exp(294/T) cm^3 molecule^{-1} s^{-1} over the temperature range 202–415 K.

Reliability
$\Delta\log k=\pm0.1$ at 298 K.
$\Delta(E/R)=\pm100$ K.

Comments on Preferred Values

The room temperature rate coefficients reported by Clyne and MacRobert,[1] Lee *et al.*,[2] Clyne and Watson,[3] Leu and DeMore,[4] and Ray and Watson[5] are in very good agreement and are averaged to yield the 298 K preferred value. The value reported by Zahniser and Kaufman[6] from a competitive study is about 30% higher. The Arrhenius expression is derived from a least squares fit to the data reported in Refs. 1–5. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[7]

References

[1] M. A. A. Clyne and A. J. MacRobert, Int. J. Chem. Kinet. **12**, 79 (1980).
[2] Y.-P. Lee, R. M. Stimpfle, R. A. Perry, J. A. Mucha, K. M. Evenson, D. A. Jennings, and C. J. Howard, Int. J. Chem. Kinet. **14**, 711 (1982).
[3] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **70**, 2250 (1974).
[4] M. T. Leu and W. B. DeMore, J. Phys. Chem. **82**, 2049 (1978).
[5] G. W. Ray and R. T. Watson, J. Phys. Chem. **85**, 2955 (1981).
[6] M. S. Zahniser and F. Kaufman, J. Chem. Phys. **66**, 3673 (1977).
[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$ClO + NO_2 + M \rightarrow ClONO_2 + M$

$\Delta H^\circ=-111.9$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
1.6×10^{-31} $(T/300)^{-3.4}$ [N$_2$]	200–300	IUPAC, 1992[1]	(a)
1.8×10^{-31} $(T/300)^{-3.4}$ [air]	200–300	NASA, 1994[2]	(b)
1.8×10^{-31} [N$_2$]	300	Rayez and Destriau, 1993[3]	(c)

Comments

(a) There is excellent agreement between various studies. The preferred value is the average of eleven different studies evaluated earlier.[4–6] The falloff curve is evaluated with $F_c=0.5$ at 298 K.

(b) Several independent low-pressure determinations are in excellent agreement.[7–10]

(c) Theoretical evaluation following Ref. 11. Using $\Delta H^\circ_0=105$ kJ mol^{-1}, $\beta_c=0.71$ is obtained; if a value $\Delta H^\circ_0=110$ kJ mol^{-1} is employed, $\beta_c=0.54$ results.

Preferred Values

$k_0=1.6\times10^{-31}$ $(T/300)^{-3.4}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability
$\Delta\log k_0=\pm0.1$ at 298 K.
$\Delta n=\pm1$.

Comments on Preferred Values

No new experimental measurements have been reported since our last evaluation, and the preferred values are identical to our previous evaluation, IUPAC, 1992.[1]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
2×10^{-11}	200–300	IUPAC, 1992[1]	(a)
1.5×10^{-11} $(T/300)^{-1.9}$	200–300	NASA, 1994[2]	(b)
4.0×10^{-12}	300	Rayez and Destriau, 1993[3]	(c)

Comments

(a) Since there are no direct measurements of k at pressures above 1 bar, k_∞, cannot be established with certainty, and theoretical predictions are no better than about a factor of 2. However, if the falloff curves below 1 atm are fitted with the given k_0, k_∞, and F_c values, this uncertainty does not influence the representation of the falloff curve.

(b) The high-pressure rate coefficient and the temperature dependence were from the model of Smith and Golden.[12] This modeling fits the data of Refs. 13 and 14.

(c) Theoretical calculations based on the method of Ref. 15. Estimations with $\Delta H^\circ_0=105$ or 110 kJ mol^{-1} lead to identical k_∞ values.

Preferred Values

$k_\infty=2\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta\log k_\infty=\pm0.3$ at 298 K.

Comments on Preferred Values

The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[1]

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).
[3] M. T. Rayez and M. Destriau, Chem. Phys. Lett. **206**, 278 (1993).
[4] CODATA, Supplement II, 1984 (see references in Introduction).
[5] IUPAC, Supplement III, 1989 (see references in Introduction).
[6] NASA Evaluation No. 9, 1990 (see references in Introduction).
[7] M. S. Zahniser, J. S. Chang, and F. Kaufman, J. Chem. Phys. **67**, 997 (1977).
[8] J. W. Birks, B. Shoemaker, T. J. Leck, R. A. Borders, and L. H. Hart, J. Chem. Phys. **66**, 4591 (1977).
[9] M. T. Leu, C. L. Lin, and W. B. DeMore, J. Phys. Chem. **81**, 190 (1977).
[10] Y.-P. Lee, R. M. Stimpfle, R. A. Perry, J. A. Mucha, K. M. Evenson, D. A. Jennings, and C. J. Howard, Int. J. Chem. Kinet. **14**, 711 (1982).
[11] J. Troe, J. Chem. Phys. **66**, 4758 (1977), J. Phys. Chem. **83**, 114 (1979).
[12] G. P. Smith and D. M. Golden, Int. J. Chem. Kinet. **10**, 489 (1978).
[13] R. A. Cox and R. Lewis, J. Chem. Soc. Faraday Trans. 1, **75**, 2649 (1979).
[14] W. Dasch, K.-H. Sternberg, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **85**, 611 (1981).
[15] J. Troe, J. Phys. Chem. NF **161**, 209 (1989).

$ClO + NO_3 \rightarrow ClOO + NO_2$ (1)
$\rightarrow OClO + NO_2$ (2)

$\Delta H^\circ(1)=-44.6$ kJ·mol^{-1}
$\Delta H^\circ(2)=-46.5$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.0\pm1.4)\times10^{-13}$	210–353	Biggs *et al.*, 1991[1]	(a)
$k_1<1\times10^{-13}$	298	Becker *et al.*, 1991[2]	(b)
$k_2=(4.3\pm1.0)\times10^{-13}$	298		
Branching Ratios			
$k_1/k=0.80\pm0.10$	297	Biggs *et al.*, 1991[1]	(a)
$k_1/k<0.20$	298	Becker *et al.*, 1991[2]	(b)
Reviews and Evaluations			
4.0×10^{-13}	298	IUPAC, 1992[3]	(c)
4.7×10^{-13}	210–350	NASA, 1994[4]	(d)

Comments

(a) Discharge flow apparatus. Pseudo-first-order decay of NO_3 in excess ClO determined by optical absorption at 662 nm. Product branching ratios were measured with a quadrupole mass spectrometer. The ratio k_2/k was determined to be 0.20±0.10 at 297 K, decreasing with decreasing temperature to a value of 0.035 at 216 K.

(b) Discharge flow-mass spectrometric technique. Rate constants were derived from numerical simulation of the ClO and OClO concentration profiles.

(c) Based on the results of Cox *et al.*[5,6]

(d) Based on the results of Biggs *et al.*,[1] Becker *et al.*,[2] and Cox *et al.*[5,6]

Preferred Values

$k=4.7\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 210–350 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm400$ K.

Comments on Preferred Values

The preferred values are based on the results reported by Cox *et al.*,[5,6] Biggs *et al.*,[1] and Becker *et al.*[2] Biggs *et al.*[1] report the rate constant to be independent of temperature, consistent with the results of Cox *et al.*[6] There is a significant discrepancy in the reported values for the branching ratio. Biggs *et al.*[1] report the major reaction channel to be that forming ClOO + NO_2 (channel 1), consistent with the results of Cox *et al.*[6] In contrast, Becker *et al.*[2] report the major channel to be that forming OClO + NO_2 (channel 2). From a study of the OClO-NO_3 system, Friedl *et al.*[7] conclude that at 220 K the major reaction channel is channel 1, in general agreement with the conclusions of Biggs *et al.*[1]

References

[1] P. Biggs, M. H. Harwood, A. D. Parr, and R. P. Wayne, J. Phys. Chem. **95**, 7746 (1991).

[2] E. Becker, U. Wille, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **95**, 1173 (1991).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

[5] R. A. Cox, R. A. Barton, E. Ljungstrom, and D. W. Stocker, Chem. Phys. Lett. **108**, 228 (1984).

[6] R. A. Cox, M. Fowles, D. Moulton, and R. P. Wayne, J. Phys. Chem. **91**, 3361 (1987).

[7] R. R. Friedl, S. P. Sander, and Y. L. Yung, J. Phys. Chem. **96**, 7490 (1992).

$ClO + ClO \rightarrow Cl_2 + O_2$ (1)
$\rightarrow Cl + ClOO$ (2)
$\rightarrow Cl + OClO$ (3)

$\Delta H^\circ(1)=-203.2$ kJ·mol^{-1}

$\Delta H^\circ(2)=15.6$ kJ·mol^{-1}

$\Delta H^\circ(3)=13.7$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2+k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_1=1.01\times10^{-12}\exp[-(1590\pm100)/T]$	260–390	Nickolaisen, Friedl, and Sander, 1994[1]	(a)
$k_2=2.98\times10^{-11}\exp[-(2450\pm330)/T]$	260–390		
$k_3=3.50\times10^{-13}\exp[-(1370\pm150)/T]$	260–390		
Branching Ratios			
$k_1/k=0.40\pm0.08$	298	Horowitz *et al.*, 1993[2]	(b)
$k_2/k=0.42\pm0.08$	298		
$k_3/k=0.18\pm0.02$	298		
Reviews and Evaluations			
$k_1=4.9\times10^{-15}$	298	IUPAC, 1992[3]	(c)
$k_2=3.4\times10^{-15}$	298		
$k_3=1.7\times10^{-15}$	298		
$k_1=1.0\times10^{-12}\exp(-1590/T)$	260–390	NASA, 1994[4]	(d)
$k_2=3.0\times10^{-11}\exp(-2450/T)$	260–390		
$k_3=3.5\times10^{-13}\exp(-1370/T)$	260–390		

Comments

(a) Flash photolysis/long path ultraviolet absorption technique. Cl_2-Cl_2O mixtures were photolyzed at wavelengths longer than 300 nm. The UV absorption of ClO and OClO were monitored with an optical multichannel analyzer. The reaction was studied over a wide range of temperature, pressure, and initial reactant stoichiometry.

(b) Cl_2 sensitized continuous photolysis of Cl_2-O_3 mixtures in excess O_2. Decay of O_3 and formation of OClO monitored by UV absorption.

(c) Based on results of Clyne *et al.*[5] and Cox and Derwent.[6]

(d) Based on results of Nickolaisen *et al.*[1]

Preferred Values

$k_1 = 4.8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2 = 8.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_3 = 3.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 1.0 \times 10^{-12} \exp(-1590/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–390 K.

$k_2 = 3.0 \times 10^{-11} \exp(-2450/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–390 K.

$k_3 = 3.5 \times 10^{-13} \exp(-1370/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–390 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \Delta \log k_3 = \pm 0.2$ at 298 K.

$\Delta(E_1/R) = \Delta(E_3/R) = \pm 300$ K; $\Delta(E_2/R) = \pm 500$ K.

Comments on Preferred Values

The recommended values for the individual reaction channels are those from the recent study of Nicholaisen *et al.*[1] This study using a flash photolysis/long path ultraviolet absorption technique is the most comprehensive study of this system, covering a wide range of temperature, initial reactant stoichiometry, and pressure. These results[1] are preferred over the results of earlier studies of the total bimolecular rate coefficient at low pressures by Clyne and co-workers[5] as discussed in reviews of Watson,[7,8] and those of other studies reported by Hayman *et al.*,[9] Cox and Derwent,[6] Simon *et al.*,[10] and Horowitz *et al.*[2] The room temperature branching ratios are $k_1:k_2:k_3 = 0.29:0.50:0.21$. The reaction exhibits both bimolecular and termolecular reaction channels. The termolecular reaction dominates at pressures higher than about 0.013 bar.

References

[1] S. L. Nickolaisen, R. R. Friedl, and S. P. Sander, J. Phys. Chem. **98**, 155 (1994).

[2] A. Horowitz, D. Bauer, J. N. Crowley, and G. K. Moortgat, Geophys. Res. Lett. **20**, 1423 (1993).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

[5] M. A. A. Clyne, D. J. McKenney, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **71**, 322 (1975).

[6] R. A. Cox and R. G. Derwent, J. Chem. Soc. Faraday Trans. 1, **75**, 1635 (1979).

[7] R. T. Watson, J. Phys. Chem. Ref. Data **6**, 871 (1977).

[8] R. T. Watson, Proceedings of the NATO Advanced Study Institute on Atmospheric Ozone, Report FAA-EE-80-20, FAA, Washington, DC (1980).

[9] G. D. Hayman, J. M. Davies, and R. A. Cox, Geophys. Res. Lett. **13**, 1347 (1986).

[10] F. G. Simon, W. Schneider, G. K. Moortgat, and J. P. Burrows, J. Photochem. Photobiol. A **55**, 1 (1990).

$ClO + ClO + M \rightarrow Cl_2O_2 + M$

$\Delta H° = 75.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.22 \times 10^{-33} \exp[(833 \pm 34)/T]$ [N_2]	195-390	Nickolaisen, Friedl, and Sander, 1994[1]	(a)
$(0.99 \pm 0.05) \times 10^{-32}$ [He]	300		
$(1.24 \pm 0.09) \times 10^{-32}$ [O_2]	300		
$(1.71 \pm 0.06) \times 10^{-32}$ [Ar]	300		
$(2.60 \pm 0.17) \times 10^{-32}$ [CF_4]	300		
$(3.15 \pm 0.14) \times 10^{-32}$ [SF_6]	300		
$(6.7 \pm 3.6) \times 10^{-32}$ [Cl_2]	300		
Reviews and Evaluations			
$1.7 \times 10^{-32} (T/300)^{-4}$ [N_2]	200–260	IUPAC, 1992[2]	(b)
$2.2 \times 10^{-32} (T/300)^{-3.1}$ [N_2]	200–300	NASA, 1994[3]	(c)

Comments

(a) Flash photolysis of Cl_2 at $\lambda > 300$ nm in the presence of Cl_2O. ClO radicals were generated by the reaction $Cl + Cl_2O \rightarrow ClO + Cl_2$ and monitored by UV absorption spectroscopy using either a photomultiplier for detection at 275.5 nm or an optical multichannel analyzer for detection over the wavelength range 270–280 nm. Below 250 K, the reaction is in the falloff regime. From a third-law analysis the value of ΔH° of $-(75.7 \pm 0.9)$ kJ mol^{-1} was derived.

(b) The recommended values are an average of the rate data of Refs. 4 and 5.

(c) Based on data in Refs. 1, 4, and 5.

Preferred Values

$k_0 = 1.7 \times 10^{-32} (T/300)^{-4} [N_2]$ cm^{-3} $molecule^{-1}$ s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 1.5$.

Comments on Preferred Values

For temperatures relevant in atmospheric chemistry the recent experiments by Nickolaisen *et al.*[1] and our previously recommended values[2] are in very good agreement. Thus, the preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6 \pm 2) \times 10^{-12}$	195–390	Nikolaisen, Friedl, and Sander, 1994[1]	(a)
Reviews and Evaluations			
5.4×10^{-12}	200–300	IUPAC, 1992[2]	(b)
$3.5 \times 10^{-12} (T/300)^{-1.0}$	200–300	NASA, 1994[3]	(c)

Comments

(a) See comment (a) for k_0. The k_∞ value was obtained from falloff data measured below 250 K.

(b) See comment (b) for k_0.

(c) See comment (c) for k_0.

Preferred Values

$k_\infty = 5.4 \times 10^{-12}$ cm^{-3} $molecule^{-1}$ s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

Comments on Preferred Values

Our earlier recommended values[2] are consistent with the recent data from Ref. 1, and the preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] S. L. Nickolaisen, R. R. Friedl, and S. P. Sander, J. Phys. Chem. **98**, 155 (1994).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] S. P. Sander, R. R. Friedl, and Y. L. Yung, Science **245**, 1095 (1989).
[5] M. Trolier, R. L. Mauldin III, and A. R. Ravishankara, J. Phys. Chem. **94**, 4896 (1990).

$Cl_2O_2 + M \rightarrow ClO + ClO + M$

$\Delta H° = 75.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$9.81\times10^{-7}\exp[-(7980\pm320)/T]$ [N_2]	260–310	Nickolaisen, Friedl, and Sander, 1994[1]	(a)
Reviews and Evaluations			
$1.35\times10^{-5}(T/300)^{-5}\exp(-8720/T)[N_2]$	200–300	IUPAC, 1992[2]	(b)
$1.7\times10^{-5}(T/300)^{-3.1}\exp(-8744/T)$ [N_2]	200–300	NASA, 1994[3]	(c)

Comments

(a) Flash photolysis of Cl_2 at $\lambda>300$ nm in the presence of Cl_2O. ClO radicals were monitored with an optical multichannel analyzer at 270–280 nm; the pressure range was 25–650 Torr. From a third-law analysis, the value of $\Delta H° = 75.7\pm0.9$ kJ mol^{-1} was derived.

(b) The preferred values were calculated from $k_0 = 1.7\times10^{-32}(T/300)^{-4}$ [N_2] cm^3 molecule^{-1} s^{-1} for the reverse reaction (Ref. 2) and the equilibrium constant from Cox and Hayman.[4] The preferred values correspond to falloff curves with $F_c = 0.6$.

(c) Calculated with the recommended k_0 value for the reverse reaction and the value of K_c from Table 3 of the NASA evaluation.

Preferred Values

$k_0 = 2.2\times10^{-18}$ [N_2] s^{-1} at 298 K.

$k_0 = 1\times10^{-6}\exp(-8000/T)$ [N_2] s^{-1} over the temperature range 260–310 K.

Reliability

$\Delta\log k_0 = \pm0.3$ at 298 K.

$\Delta(E/R) = \pm900$ K.

Comments on Preferred Values

The preferred value is based on the results of Ref. 1 and is in good agreement with the values from our previous evaluation.[2]

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.8\times10^{15}\exp(-8820/T)$	260–310	Nickolaisen, Friedl, and Sander, 1994[1]	(a)
Reviews and Evaluations			
$1.8\times10^{15}\exp(-8450/T)$	200–300	IUPAC, 1992[2]	(b)
$2.7\times10^{15}(T/300)^{-1.0}\exp(-8744/T)$	200–300	NASA, 1994[3]	(c)

Comments

(a) See comment (a) for k_0. This value is based on the rate coefficient $k_\infty = 6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} for the reverse reaction and the equilibrium constant $K_c = 1.24\times10^{-27}\exp(8820/T)$ cm^3 molecule^{-1}, both from Ref. 1.

(b) Based on the preferred value $k_\infty = 5.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} for the reverse reaction and K_c from Cox and Hayman.[4]

(c) Calculated with the recommended k_∞ value for the reverse reaction and the value of K_c from Table 3.[3]

Preferred Values

$k_\infty = 6.7\times10^{2}$ s^{-1} at 298 K.

$k_\infty = 4.8\times10^{15}\exp(-8820/T)$ s^{-1} over the temperature range 260–310 K.

Reliability

$\Delta\log k_\infty = \pm0.3$.

$\Delta(E/R) = \pm500$ K.

Comments on Preferred Values

The values of Nickolaisen *et al.*[1] are adopted here.

References

[1] S. L. Nickolaisen, R. R. Friedl, and S. P. Sander, J. Phys. Chem. **98**, 155 (1994).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] R. A. Cox and G. D. Hayman, Nature **332**, 796 (1988).

$ClO + OClO + M \rightarrow Cl_2O_3 + M$

$\Delta H° = -44$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.2\pm1.0)\times10^{-32}(T/300)^{-4.7}$ [N_2]	200–260	Burkholder *et al.*, 1993[1]	(a)
Reviews and Evaluations			
2.8×10^{-31} [N_2]	226	IUPAC, 1992[2]	(b)

Comments

(a) Flash photolysis study of mixtures of N_2O-Cl_2-OClO-He or CF_2Cl_2-OClO-N_2 at 193 nm. From the first mixture, rate data were obtained while from the second mixture equilibrium constants and the absorption spectra of Cl_2O_3 between 220 and 320 nm were derived. From a second-law analysis of the data, together with those of Hayman and Cox,[3] $\Delta H° = -(46.4\pm5.1)$ kJ mol^{-1} and $\Delta S° = -(88.7\pm18.9)$ J mol^{-1} K^{-1} were derived. The kinetic data were obtained from a fit of the falloff curves between 25–250 Torr total pressure using $F_c = 0.6$.

(b) Based on the measurements of Parr *et al.*[4]

Preferred Values

$k_0 = 6.2\times10^{-32}\ (T/300)^{-4.7}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_0 = \pm0.3$ at 298 K.
$\Delta n = \pm1$.

Comments on Preferred Values

The values of the extensive study of Burkholder *et al.*[1] are adopted here. At 226 K the rate coefficient of Ref. 1 is in reasonable agreement with that recommended previously.[2]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.4\pm1.2)\times10^{-11}$	200–260	Burkholder *et al.*, 1993[1]	(a)

Comments

(a) See comment (a) for k_0.

Preferred Values

$k_\infty = 2.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta\log k_\infty = \pm0.3$ at 298 K.

Comments on Preferred Values

The preferred values are from Ref. 1.

References

[1] J. B. Burkholder, R. L. Mauldin III, R. J. Yokelson, S. Solomon, and A. R. Ravishankara, J. Phys. Chem. **97**, 7597 (1993).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] G. D. Hayman and R. A. Cox, Chem. Phys. Lett. **155**, 1 (1989).
[4] A. D. Parr, R. P. Wayne, G. D. Hayman, M. E. Jenkin, and R. A. Cox, Geophys. Res. Lett. **17**, 2357 (1990).

$Cl_2O_3 + M \rightarrow ClO + OClO + M$

$\Delta H^\circ = 44$ kJ·mol^{-1}

Low-pressure rate coefficients

No direct measurements are available.

Preferred Values

$k_0 = 2.8 \times 10^{-18}$ [N_2] s^{-1} at 226 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 226 K.

Comments on Preferred Values

This value is calculated from the rate coefficient of the reverse reaction, $k_0 = 2.8 \times 10^{-31}$ [N_2] cm^3 molecule^{-1} s^{-1} at 226 K from Ref. 1, and the equilibrium constant $K_c = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} at 226 K from Ref. 2. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[2]

References

[1] A. D. Parr, R. P. Wayne, G. D. Hayman, M. E. Jenkin, and R. A. Cox, Geophys. Res. Lett. **17**, 2357 (1990).

[2] G. D. Hayman and R. A. Cox, Chem. Phys. Lett. **155**, 1 (1989).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$ClO + CH_3O_2 \rightarrow ClOO + CH_3O$ (1)
$\rightarrow CH_3OCl + O_2$ (2)
$\rightarrow OClO + CH_3O$ (3)

$\Delta H^\circ(1) = 3.1$ kJ·mol^{-1}
$\Delta H^\circ(3) = 1.2$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.25 \times 10^{-12} \exp[-(114 \pm 38)/T]$	225–355	Helleis, Crowley, and Moortgat, 1993[1]	(a)
2.22×10^{-12}	295		
$(1.9 \pm 0.4) \times 10^{-12}$	293	Kenner, Ryan, and Plumb, 1993[2]	(b)
Branching Ratios			
$k_1/k = 1.51 \exp[-(218 \pm 93)/T]$	225–355	Helleis, Crowley, and Moortgat, 1993[1]	(a)
$k_2/k = 0.08 \exp[(377 \pm 178)/T]$	225–355		
Reviews and Evaluations			
$k_1 < 4 \times 10^{-12}$	200	IUPAC, 1992[3]	(c)
$k_3 < 1 \times 10^{-15}$	200		
$k_1 = 4.9 \times 10^{-12} \exp(-330/T)$	200–355	NASA, 1994[4]	(d)
$k_2 = 2.6 \times 10^{-13} \exp(260/T)$	200–355		

Comments

(a) Discharge flow-mass spectrometer technique. Pseudo-first-order decay of CH_3O_2 radicals in excess ClO monitored at m/e=47. Overall rate constant and branching ratios were found to be independent of pressure.

(b) Flow reactor with quadrupole mass spectrometer sampling. Decays of CH_3O_2 radicals were monitored at m/e=47.

(c) Upper limits based on the results of DeMore.[5]

(d) Based on the results of Helleis *et al.*[1]

Preferred Values

$k_1 = 1.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$= 4.9 \times 10^{-12} \exp(-330/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 225–355 K.
$k_2 = 6.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$= 2.6 \times 10^{-13} \exp(260/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 225–355 K.
$k_3 < 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 200 K.

Reliability

$\Delta\log k_1=\Delta\log k_2=\pm 0.3$ at 298 K.

$\Delta(E_1/R)=\pm 200$ K.

$\Delta(E_2/R)=\pm 250$ K.

Comments on Preferred Values

The recommended expressions for the individual reaction channels are derived from the temperature dependent expressions for the overall rate constant and the branching ratios reported by Helleis *et al.*[1] These results are consistent with the overall rate constant measurements of Kenner *et al.*[2] and Simon *et al.*[6] at room temperature and with the upper limit for k_1 at 200 K reported by DeMore.[5] The upper limit for k_3 is based on the results of DeMore[5] and is consistent with the observations of Helleis *et al.*[1] that only reaction channels (1) and (2) are important. The recommended Arrhenius expressions yield approximately equal rate constants of 1×10^{-12} cm^3 molecule^{-1} s^{-1} for k_1 and k_2 at 200 K.

References

[1] F. Helleis, J. N. Crowley, and G. K. Moortgat, J. Phys. Chem. **97**, 11464 (1993).

[2] R. D. Kenner, K. R. Ryan, and I. C. Plumb, Geophys. Res. Lett. **20**, 1571 (1993).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

[5] W. B. DeMore, J. Geophys. Res. **96**, 4995 (1991).

[6] F. G. Simon, J. P. Burrows, W. Schneider, G. K. Moortgat, and P. J. Crutzen, J. Phys. Chem. **93**, 7807 (1989).

$ClO + CH_3SCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.9\pm0.5)\times10^{-14}$	298	Barnes *et al.*, 1989[1]	(a)
$(9.5\pm2.0)\times10^{-15}$	298	Barnes *et al.*, 1991[2]	(a)
Reviews and Evaluations			
9.5×10^{-15}	298	NASA, 1994[3]	(b)

Comments

(a) Fast flow discharge system used. ClO radicals were produced by the reaction $Cl + O_3 \rightarrow ClO + O_2$. [ClO] was monitored by mass spectrometry.

(b) Based on the rate coefficient of Barnes *et al.*[2]

Preferred Values

$k=9\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm 0.5$ at 298 K.

Comments on Preferred Values

The two available measurements[1,2] of this rate coefficient come from the same laboratory using basically the same technique. In the earlier study,[1] wall effects were evident and it was recognized that the value of k obtained was likely to be an upper limit. Better control of wall effects was obtained in the later study,[2] and the value found there is taken as the preferred value but with substantial error limits.

The reaction is usually assumed to produce $CH_3S(O)CH_3$ + Cl but, although the sulfoxide has been detected,[1] no yields have been measured.

References

[1] I. Barnes, K. H. Becker, D. Martin, P. Carlier, G. Mouvier, J. L. Jourdain, G. Laverdet, and G. Le Bras, *Biogenic Sulfur in the Environment*, edited by E. S. Saltzman and W. J. Cooper, ACS Symposium Series, No. 393, p. 464 (1989).

[2] I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, Int. J. Chem. Kinet. **23**, 579 (1991).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$OClO + O_3 \rightarrow ClO_3 + O_2$

$\Delta H^\circ=-5.7$ $\text{kJ}\cdot\text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 3.0 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.1 \times 10^{-12} \exp(-4700/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 262–298 K.

Reliability
$\Delta \log k = \pm 0.4$ at 298 K.
$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values

The preferred value is based on the results reported in the study of Wongdontri-Stuper *et al.*[1] Within the indicated uncertainty limits, the preferred values encompass the lower room temperature value reported by Birks *et al.*[2] The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] W. Wongdontri-Stuper, R. K. M. Jayanty, R. Simonaitis, and J. Heicklen. J. Photochem. **10**, 163 (1979).
[2] J. W. Birks, B. Shoemaker, T. J. Leck, R. A. Borders, and L. J. Hart, J. Chem. Phys. **66**, 4591 (1977).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$OClO + NO \rightarrow NO_2 + ClO$

$\Delta H° = -51.1$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 3.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the only direct study of this reaction reported by Bemand *et al.*[1] In the absence of experimental data no recommendation is given for the temperature dependence. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.[2]

References

[1] P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **69**, 1356 (1973).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$OClO + NO_3 + M \rightarrow O_2ClONO_2 + M$

$\Delta H° = -75$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1×10^{-31} [He]	220	Friedl, Sander, and Yung, 1992[1]	(a)

Comments

(a) The experiments were carried out in a long-path absorption flow reactor. NO_3 radicals were generated by the reaction of F atoms with HNO_3 or of Cl atoms with $ClONO_2$. The products were analyzed by IR and UV absorption measurements. At $T < 230$ K the formation of O_2ClONO_2 dominated while at higher temperatures ClO and NO_2 were also observed, indicating the presence of secondary reactions. The k_0 value was derived from a measured rate constant of 2×10^{-14} cm^3 molecule^{-1} s^{-1} at 4 Torr of He. Using unimolecular rate theory[2] and the experimental parameters, the bond dissociation energy given above was derived (± 13 kJ mol^{-1}).

Preferred Values

$k_0 = 1 \times 10^{-31}$ [He] cm^3 molecule^{-1} s^{-1} at 220 K.

Reliability
$\Delta \log k_0 = \pm 0.4$ at 220 K.

Comments on Preferred Values

The recommended values are based on the measurements of Friedl *et al.*[1]

References

[1] R. R. Friedl, S. P. Sander, and Y. L. Yung, J. Phys. Chem. **96**, 7490 (1992).
[2] J. Troe, J. Phys. Chem. **83**, 114 (1979).

$Cl_2O_2 + O_3 \rightarrow ClO + ClOO + O_2$

$\Delta H^\circ = -71.2$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k < 1 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 200 K.

Comments on Preferred Values

The recommended upper limit is that determined by DeMore and Tschuikow-Roux[1] from measurement of the quantum yield of O_3 loss in the photolysis of Cl_2-O_3 mixtures at $\lambda > 300$ nm. The experiments were very sensitive to this reaction. Reaction at a rate greater than this upper limit would have had a marked effect on the quantum yield of ozone loss and also would have resulted in a dependence of the quantum yield on the ozone concentration; however, neither effect was observed.[1] These measurements refer to a temperature of about 200 K; the value of this rate coefficient at higher temperatures would be of no atmospheric significance because of the thermal decomposition of the Cl_2O_2 dimer. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.[2]

References

[1] W. B. DeMore and E. Tschuikow-Roux, J. Phys. Chem. **94**, 5856 (1990).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CF_2Cl + O_2 + M \rightarrow CF_2ClO_2 + M$

$\Delta H^\circ = -127.4$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.4 \times 10^{-29} (T/300)^{-5} [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

There are no measurements for this reaction, but theoretical modeling of the complete series[1] $CX_3 + O_2 + M$ (X =F, Cl) provides a reliable basis for interpolating rate data between members of this series.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ over the temperature range 200–300 K.

Comments on Preferred Values

We prefer a slightly higher value than estimated in Ref. 1. These preferred values are chosen as for the related reaction $CFCl_2 + O_2 + M$ (see this evaluation), based on data from Ref. 2. F_c=0.6 is recommended as for $CFCl_2 + O_2 + M$. $\Delta H°$ is estimated following Ref. 1. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] W. Forst and F. Caralp, J. Chem. Soc. Faraday Trans. **87**, 2307 (1991).
[2] F. Danis, Ph.D. Thesis, Bordeaux, 1990, cited in Ref. 1.
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CFCl_2 + O_2 + M \rightarrow CFCl_2O_2 + M$

$\Delta H° = -124.6\ kJ \cdot mol^{-1}$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 5.5 \times 10^{-30}\ (T/300)^{-6}\ [N_2]\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 2$.

Comments on Preferred Values

The preferred values are based on Ref. 1. The data appear consistent with other results for the series $CX_3 + O_2 + M$ (X=Cl, F) (see this evaluation).

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 9 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

Experiments have been limited to the lower part of the falloff curve. Therefore, the extrapolation to the high pressure limit remains relatively uncertain. The more recent value from Ref. 1 is preferred because it is close to the k_∞ value for the reaction $CF_3 + O_2 + M$ (see this evaluation). The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[2]

References

[1] F. Danis, Ph.D. Thesis, Bordeaux, 1990, cited in Ref. 2.
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$

$\Delta H° = -82.4$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.5\pm0.2)\times10^{-31}(T/300)^{-6.1\pm0.2}$ [He]	298–333	Fenter *et al.*, 1993[1]	(a)
Reviews and Evaluations			
$1.6\times10^{-30}\ (T/300)^{-6}$ [N_2]	200–300	IUPAC, 1992[2]	(b)
$6.9\times10^{-31}\ (T/300)^{-6.4}$ [N_2]	200–300	NASA, 1994[3]	(c)

Comments

(a) Photolysis of CCl_3Br at 248 nm with detection of CCl_3 either by mass spectrometry or by UV absorption at 215 nm. In the first case, N_2 pressures were varied between 1–12 Torr and in the second case between 20–760 Torr N_2. The derived k_0 values at 298 and 333 were obtained from a falloff fit using $F_c=0.6$.

(b) The preferred values are based on Ref. 4, and are consistent with the data for M=He from Ref. 5. The falloff curves are extrapolated with $F_c=0.6$.

(c) Based on the data from Refs. 1 and 4.

Preferred Values

$k_0=9\times10^{-31}\ (T/300)^{-6}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_0=\pm0.3$ at 298 K.

$\Delta n=\pm1$.

Comments on Preferred Values

The preferred values are based on the data of Refs. 1, 4, and 5. The values of k_0 in Refs. 1 and 5 were determined using $F_c=0.6$.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.6\pm0.2)\times10^{-12}(T/300)^{-1.1\pm0.6}$	298–333	Fenter *et al.*, 1993[1]	(a)
Reviews and Evaluations			
3.6×10^{-12}	200–300	IUPAC, 1992[2]	(b)
$2.4\times10^{-12}\ (T/300)^{-2.1}$	200–300	NASA, 1994[3]	(c)

Comments

(a) See comment (a) for k_0.

(b) The preferred values are an average of the data from Refs. 4–6.

(c) See comment (c) for k_0.

Preferred Values

$k_\infty=3\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta\log k_\infty=\pm0.4$ over the temperature range 200–300 K.

Comments on Preferred Values

Preferred values are based on the results of Refs. 1 and 4–6.

References

[1] F. F. Fenter, P. D. Lightfoot, J. T. Niiranen, and D. Gutman, J. Phys. Chem. 97, 5313 (1993).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] F. Danis, F. Caralp, M. T. Rayez, and R. Lesclaux, J. Phys. Chem. 95, 7300 (1991).
[5] K. R. Ryan and I. C. Plumb, Int. J. Chem. Kinet. 16, 591 (1984).
[6] R. Cooper, J. B. Cumming, S. Gordon, and W. A. Mulac, Rad. Phys. Chem. 16, 169 (1980).

$CF_2ClO_2 + NO_2 + M \rightarrow CF_2ClO_2NO_2 + M$

$\Delta H^\circ = -107\ kJ \cdot mol^{-1}$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.4 \times 10^{-28}\ (T/300)^{-6.4}\ [N_2]\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.
$\Delta n = \pm 2$.

Comments on Preferred Values

The preferred values are from Ref. 1, and are consistent with data for the reactions $CCl_3O_2 + NO_2$ and $CFCl_2O_2 + NO_2$. These values are sensitive to the chosen value of F_c, for which a value of 0.26 was calculated[1] over the range 220–300 K. The values from Ref. 2 in part are lower because of the larger value of F_c used.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 7.5 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

The preferred values are from the fit in Ref. 1 using identical k_∞ values for all $CX_3O_2 + NO_2$ reactions (X=F, Cl), independent of the temperature. The large negative temperature coefficient of k_∞ reported in Ref. 2 appears to be an artifact from the falloff extrapolations used. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[2] F. Wu and R. W. Carr, Int. J. Chem. Kinet. **23**, 701 (1991).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CF_2ClO_2NO_2 + M \rightarrow CF_2ClO_2 + NO_2 + M$

$\Delta H^\circ = 107\ kJ \cdot mol^{-1}$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 9.0 \times 10^{-19}\ [N_2]\ s^{-1}$ at 298 K.
$k_0 = 1.8 \times 10^{-3} \exp(-10500/T)\ [N_2]\ s^{-1}$ over the temperature range 260–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The data from the experiments of Ref. 1 are preferred here. The calculations of F_c (0.3 at 280 K from Ref. 1 and 0.26 over the range 250–300 K from Ref. 2) are in agreement.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 5.4 \times 10^{-2}$ s^{-1} at 298 K.
$k_\infty = 1.6 \times 10^{16} \exp(-11990/T)$ s^{-1} over the temperature range 260–300 K.

Reliability
$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta \log (E/R) = \pm 500$ K.

Comments on Preferred Values

See comments on k_0. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] D. Köppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).
[2] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CFCl_2O_2 + NO_2 + M \rightarrow CFCl_2O_2NO_2 + M$

$\Delta H° = -106$ kJ·mol−1

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.7 \times 10^{-28} (T/300)^{-6.7} [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–300 K.

Reliability
$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 2$.

Comments on Preferred Values

The preferred values are from the analysis of Ref. 1 on the basis of $F_c = 0.23$. The falloff data from Ref. 2 show some anomalies for $T = 233$ K. The best fit is obtained for 298 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–300 K.

Reliability
$\Delta \log k_\infty = \pm 0.3$ over the temperature range 250–300 K.

Comments on Preferred Values

See comments on k_0. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[2] F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2, **84**, 569 (1988).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CFCl_2O_2NO_2 + M \rightarrow CFCl_2O_2 + NO_2 + M$

$\Delta H° = 106$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.5 \times 10^{-18}$ [N_2] s^{-1} at 298 K.
$k_0 = 1.0 \times 10^{-2} \exp(-10860/T)$ [N_2] s^{-1} over the temperature range 250–300 K.

Reliability
$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The data from the experiments of Ref. 1 are preferred. The calculation of $F_c = 0.28$ is consistent with the analysis of Ref. 2, leading to $F_c = 0.23$.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 9.6 \times 10^{-2}$ s^{-1} at 298 K.
$k_\infty = 6.6 \times 10^{16} \exp(-12240/T)$ s^{-1} over the temperature range 250–300 K.

Reliability
$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

See comments on k_0. The agreement between Refs. 1 and 3 at 1 atm ($\Delta \log k = 0.17$) appears satisfactory. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] D. Köppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).
[2] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[3] R. Simonaitis, S. Glavas, and J. Heicklen, Geophys. Res. Lett. **6**, 385 (1979).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CCl_3O_2 + NO_2 + M \rightarrow CCl_3O_2NO_2 + M$

$\Delta H° = -105.6$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 3.2 \times 10^{-28} (T/300)^{-7.7}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 230–300 K.

Reliability
$\Delta \log k_0 = \pm 0.5$ at 298 K.
$\Delta n = \pm 3$.

Comments on Preferred Values

The preferred values are from the theoretical analysis of Ref. 1. The experimental data from Ref. 2 for $T = 233$ K apparently are inconsistent with this analysis. $F_c = 0.21$ is used for falloff extrapolations.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 250–300 K.

Comments on Preferred Values

The value of k_∞ in Ref. 1 was chosen identical for all reactions $CX_3O_2 + NO_2 + M$ (X=F, Cl), which leads to a consistent set of falloff curves. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.[3]

References

[1] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).

[2] F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2, **84**, 569 (1988).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CCl_3O_2NO_2 + M \rightarrow CCl_3O_2 + NO_2 + M$

$\Delta H^\circ = 105.6$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 7.6 \times 10^{-18}$ [N$_2$] s^{-1} at 298 K.

$k_0 = 6.3 \times 10^{-3} \exp(-10235/T)$ [N$_2$] s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The experimental data of Ref. 1 are recommended. The calculation of $F_c = 0.22$ is consistent with the analysis of Ref. 2, which gave $F_c = 0.20$ with only a weak temperature dependence.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 0.29$ s^{-1} at 298 K.

$k_\infty = 4.8 \times 10^{16} \exp(-11820/T)$ s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

See comments on k_0. The agreement between Refs. 1 and 3 for 1 atm total pressure ($\Delta \log k = 0.11$) appears satisfactory. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] D. Köppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).

[2] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).

[3] R. Simonaitis and J. Heicklen, Chem. Phys. Lett. **62**, 473 (1979); **68**, 245 (1979).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$$C_2H_5O_2 + CF_3CCl_2O_2 \rightarrow CH_3CHO + CF_3CCl_2OH + O_2 \quad (1)$$

$$\rightarrow C_2H_5O + CF_3CCl_2O + O_2 \quad (2)$$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_1=(3.6\pm0.5)\times10^{-12}$	298	Hayman *et al.*, 1994[1]	(a)
$k_2=(9^{+6}_{-5})\times10^{-13}$	298		

Comments

(a) Laser flash photolysis-UV absorption study of CF_3CCl_3-C_2H_6-O_2-N_2 mixtures. Kinetic data were obtained by analyzing two sets of transient decays on the basis of a mechanism consisting of 13 reactions.

Preferred Values

$k_1=3.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2=9\times10^{-13}$ molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k_1=\pm0.3$ at 298 K.
$\Delta\log k_2=\pm0.5$ at 298 K.

Comments on Preferred Values

While the above values of the rate coefficients[1] appear reasonable, they have been derived from the analysis of a complex chemical system and require independent verification to reduce the recommended error limits.

References

[1] G. D. Hayman, M. E. Jenkin, T. P. Murrells, and C. E. Johnson, Atmos. Environ. **28A**, 421 (1994).

$$CF_2ClCH_2O_2 + CF_2ClCH_2O_2 \rightarrow CF_2ClCH_2OH + CF_2ClCHO + O_2 \quad (1)$$

$$\rightarrow 2CF_2ClCH_2O + O_2 \quad (2)$$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq4.1\times10^{-12}$	298	Wallington and Nielsen, 1991[1]	(a,b)
Reviews and Evaluations			
$\leq4.1\times10^{-12}$	298	Lightfoot *et al.*, 1992[2]	(c)

Comments

(a) k is defined by $-d[CF_2ClCH_2O_2]/dt=2k[CF_2ClCH_2O_2]^2$ and has been derived from the measured overall second-order decay of $CF_2ClCH_2O_2$ radicals (k_{obs}).

(b) Pulse radiolysis study of CF_2ClCH_3-O_2-SF_6 mixtures over the pressure range 114–760 Torr. $CF_2ClCH_2O_2$ radicals were monitored by UV absorption with $\sigma_{250}=(3.38\pm0.68)\times10^{-18}$ cm^2 molecule^{-1}. The derived value of $k_{obs}=(4.1\pm0.6)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} is an upper limit to k (see Comments on Preferred Values).

(c) Based on the data of Wallington and Nielsen.[1]

Preferred Values

$k\leq4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

We have recommended a rounded-off upper limit for the rate coefficient at 298 K as determined by Wallington and Nielsen.[1] It has been noted[2] that this system has also been studied by Jemi-Alade *et al.*,[3] using a flash photolysis-UV absorption technique. Although no rate coefficients were obtained, a strong residual absorption was observed, indicating a complex chemical system with the probability of secondary removal of $CF_2ClCH_2O_2$ radicals. No product studies have been reported on this reaction and consequently the branching ratio is unknown.

References

[1] T. J. Wallington and O. J. Nielsen, Int. J. Chem. Kinet. 23, 785 (1991).
[2] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. 26A, 1805 (1992).
[3] A. A. Jemi-Alade, P. D. Lightfoot, and R. Lesclaux, Chem. Phys. Lett. 179, 119 (1991).

$CFCl_2CH_2O_2 + CFCl_2CH_2O_2 \rightarrow CFCl_2CH_2OH + CFCl_2CHO + O_2$ (1)
$\rightarrow 2CFCl_2CH_2O + O_2$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 4.4\times10^{-12}$	298	Wallington and Nielsen, 1991[1]	(a,b)
Reviews and Evaluations			
$\leq 4.1\times10^{-12}$	298	Lightfoot *et al.*, 1992[2]	(c)

Comments

(a) k is defined by $-d[CFCl_2CH_2O_2]/dt = 2k[CFCl_2CH_2O_2]^2$ and has been derived from the measured overall second-order decay of $CFCl_2CH_2O_2$ radicals (k_{obs}).

(b) Pulse radiolysis study of $CFCl_2CH_3$-O_2-SF_6 mixtures over the pressure range 114–760 Torr. $CFCl_2CH_2O_2$ radicals were monitored by UV absorption with $\sigma_{230}=(3.38\pm0.68)\times10^{-18}$ cm^2 molecule^{-1}. The derived value of $k_{obs}=(4.36\pm0.64)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} is an upper limit to k (see Comments on Preferred Values).

(c) Based on the data of Wallington and Nielsen,[1] but scaled to an evaluated value[2] of σ_{230} ($CFCl_2CH_2O_2$).

Preferred Values

$k \leq 4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

We have recommended a rounded-off upper limit for the rate coefficient at 298 K as determined by Wallington and Nielsen.[1] It has been noted[2] that this system has also been studied by Jemi-Alade *et al.*,[3] using a flash photolysis-UV absorption technique. Although no rate coefficients were obtained, a strong residual absorption was observed, indicating a complex chemical system with the probability of secondary removal of $CFCl_2CH_2O_2$ radicals. No product studies have been reported on this reaction and consequently the branching ratio is unknown.

References

[1] T. J. Wallington and O. J. Nielsen, Int. J. Chem. Kinet. 23, 785 (1991).
[2] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. 26A, 1805 (1992).
[3] A. A. Jemi-Alade, P. D. Lightfoot, and R. Lesclaux, Chem. Phys. Lett. 179, 119 (1991).

$CF_3CCl_2O_2 + CF_3CCl_2O_2 \rightarrow CF_3CCl_2OOCCl_2CF_3 + O_2$ (1)
$\rightarrow 2CF_3CCl_2O + O_2$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 3.3\times10^{-12}$	295	Wallington, Ellermann, and Nielsen, 1994[1]	(a,b)
Branching Ratios			
$k_2/k \approx 1.0$	296	Edney, Gay, and Driscoll, 1991[2]	(c)
$k_2/k \approx 1.0$	298	Tuazon and Atkinson, 1993[3]	(d)
$k_2/k \approx 1.0$	298	Hayman *et al.*, 1994[4]	(e)

Comments

(a) k is defined by $-d[CF_3CCl_2O_2]/dt=2k[CF_3CCl_2O_2]^2$ and has been derived from the measured overall second-order decay of $CF_3CCl_2O_2$ radicals (k_{obs}).

(b) Pulse radiolysis study of CF_3CHCl_2-O_2-SF_6 mixtures at a total pressure of 760 Torr. $CF_3CCl_2O_2$ radicals were monitored by UV absorption with $\sigma_{250}=(1.70\pm0.26)\times10^{-18}$ cm^2 molecule^{-1}. The derived value of $k_{obs}=(3.33\pm0.53)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} is an upper limit to k (see Comments on Preferred Values).

(c) Steady-state photolysis of Cl_2 in the presence of CF_3CHCl_2-air mixtures with FTIR absorption spectroscopic analysis. $\sim$100% conversion of CF_3CHCl_2 to CF_3COCl was observed, consistent with channel (2) as the sole route for the self-reaction of $CF_3CCl_2O_2$ radicals.

(d) Similar experiments to those of Comment (c), with 98% conversion of CF_3CHCl_2 to CF_3COCl being observed.

(e) Similar experiments to those of Comment (c), with analysis by multichannel UV absorption spectroscopy. $\sim$100% conversion of CF_3CHCl_2 to CF_3COCl was observed.

Preferred Values

$k_2\leqslant3\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k=1.0$ at 298 K.

Reliability

$\Delta(k_2/k)=\pm0.05$ at 298 K.

Comments on Preferred Values

The product studies[2-4] have confirmed the absence of the formation of any $CF_3CCl_2OOCCl_2CF_3$ product and are consistent with reaction (2) being the sole pathway for the self-reaction of $CF_3CCl_2O_2$ radicals.

We have recommended a rounded-off upper limit for the rate coefficient at 298 K, as determined by Wallington *et al.*[1] A study of $CF_3CCl_2O_2$ reactions by Jemi-Alade *et al.*,[5] involving flash photolysis-UV absorption of Cl_2 in the presence of CF_3CHCl_2 and O_2, showed no decay in the absorption curves of $CF_3CCl_2O_2$ over the time scale 0–40 min. This was attributed to the regeneration of $CF_3CCl_2O_2$ via Cl atom reactions. In the Wallington *et al.*[1] study which involved concentrations of $CF_3CCl_2O_2$ radicals an order of magnitude higher than the Jemi-Alade *et al.*[2] system, the UV absorptions of the radical showed significant decays over the time scale 0–1000 ms. Until the chemistry of both these systems is better understood the k_{obs} value from the second-order decay of $CF_3CCl_2O_2$ radicals observed by Wallington *et al.*[1] must be taken as an upper limit.

References

[1] T. J. Wallington, T. Ellermann, and O. J. Nielsen, Res. Chem. Intermed. **20**, 265 (1994).
[2] E. O. Edney, B. W. Gay, Jr., and D. J. Driscoll, J. Atmos. Chem. **12**, 105 (1991).
[3] E. C. Tuazon and R. Atkinson, J. Atmos. Chem. **17**, 179 (1993).
[4] G. D. Hayman, M. E. Jenkin, T. P. Murrells, and C. E. Johnson, Atmos. Environ. **28A**, 421 (1994).
[5] A. A. Jemi-Alade, P. D. Lightfoot, and R. Lesclaux, Chem. Phys. Lett. **179**, 119 (1991).

$$
\begin{aligned}
CH_2ClO_2 + CH_2ClO_2 &\rightarrow CH_2ClOH + HCOCl + O_2 \quad (1)\\
&\rightarrow 2CH_2ClO + O_2 \quad (2)
\end{aligned}
$$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_2\leqslant3.1\times10^{-13}\exp(735/T)$	228–380	Dagaut, Wallington, and Kurylo, 1988[1]	(a,b)
$k_2\leqslant3.8\times10^{-12}$	298		
$k_2=1.95\times10^{-13}\exp[(874\pm26)/T]$	251–600	Catoire *et al.*, 1994[2]	(a,c)
$k_2=(4.2\pm0.4)\times10^{-12}$	298		
Branching Ratios			
$k_2/k\approx1.0$	305	Sanhueza and Heicklen, 1975[3]	(d)
$k_2/k\approx1.0$	298	Niki *et al.*, 1980[4]	(e)
Reviews and Evaluations			
$k_{obs}=3.9\times10^{-13}\exp(735/T)$	228–380	Lightfoot *et al.*, 1992[5]	(f)

Comments

(a) k is defined by $-d[CH_2ClO_2]/dt=2k[CH_2ClO_2]^2$ and has been derived from the measured overall second-order decay of CH_2ClO_2 radicals (k_{obs}).

(b) Flash photolysis of Cl_2 in the presence of CH_3Cl-O_2-N_2 mixtures at total pressures of 25–400 Torr at 298 K and of 100 Torr (N_2) from 228–380 K. The peroxy radicals were monitored by UV absorption with $\sigma_{250}=(3.14\pm0.45)\times10^{-18}$ cm^2 molecule^{-1}. The derived value of k_{obs} is an upper limit to k_2, because of the possibility of secondary reactions producing an enhanced decay of CH_2ClO_2 radicals (see Comments on Preferred Values).

(c) Similar experiments to those in Comment (b) at a total pressure of 760 Torr and with peroxy radical concentrations being monitored by UV absorption spectrometry from 205 to 290 nm. Values of k_{obs} were found to be markedly dependent on the monitoring wavelength, since the $RO_2 + HO_2$ reaction is not much faster than that for $RO_2 + RO_2$, leading to significant concentrations of HO_2 radicals. Values of k_2 were obtained by an iterative process.

(d) Photolysis of Cl_2 in the presence of CH_3Cl-O_2 mixtures. *In situ* monitoring of products by IR showed exclusive formation of HCl and HCOCl as the initial products.

(e) Photolysis of Cl_2 in the presence of CH_3Cl-air mixtures. *In situ* monitoring of reactants and products by FTIR spectroscopy showed 90–95% conversion of CH_3Cl to HCOCl.

(f) Based on the data of Dagaut *et al.*,[1] but scaled to an amended value of $\sigma_{250}=3.91\times10^{-18}$ cm^2 molecule^{-1} for the CH_2ClO_2 radical.

Preferred Values

$k_2=3.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2=2.0\times10^{-13}\exp(870/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–600 K.

Reliability

$\Delta\log k_2=\pm0.2$ at 298 K.
$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The product studies[3,4] have shown that the radical forming reaction (2) is the only important channel for the self-reaction of CH_2ClO_2 radicals.

The above recommendations are based on the more comprehensive study of Catoire *et al.*[2] This showed excellent agreement with the earlier data of Dagaut *et al.*[1] when both sets of data were analyzed by a simple second-order treatment from results derived at $\lambda=250$ nm. Catoire *et al.*[2] have also shown that the rate coefficient of the $CH_2ClO_2 + HO_2$ reaction is of similar magnitude to that of k_2. This leads to the presence of significant concentrations of HO_2 radicals in the system, shown by variation of k_{obs} with monitoring λ, and means that the value of k_2 cannot be obtained simply from k_{obs} and a knowledge of the branching ratio. The rate coefficients of Catoire *et al.*,[2] obtained by numerical modeling of the system, are consequently preferred.

References

[1] P. Dagaut, T. J. Wallington, and M. J. Kurylo, Int. J. Chem. Kinet. **20**, 815 (1988).
[2] V. Catoire, R. Lesclaux, P. D. Lightfoot, and M.-T. Rayez, J. Phys. Chem. **98**, 2889 (1994).
[3] E. Sanhueza and J. Heicklen, J. Phys. Chem. **79**, 7 (1975).
[4] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **12**, 1001 (1980).
[5] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).

$CCl_3O_2 + CCl_3O_2 \rightarrow CCl_3OOCCl_3 + O_2$ (1)
$\rightarrow 2CCl_3O + O_2$ (2)

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.6\times10^{-12}(T/298)^{-3.0}$	253–333	Russell *et al.*, 1990[1]	(a,b)
Branching Ratios			
$k_2/k=1.0$	298	Jayanty, Simonaitis, and Heicklen, 1975[2]	(c)
$k_2/k=1.0$	296	Ohta and Mizoguchi, 1980[3]	(d)
Reviews and Evaluations			
$8.9\times10^{-14}\exp(859/T)$	253–333	Lightfoot *et al.*, 1992[4]	(e)

Comments

(a) k is defined by $-d[CCl_3O_2]/dt=2k[CCl_3O_2]$.[2]

(b) Flash photolysis of Cl_2 in the presence of $CHCl_3$-O_2-N_2 mixtures at 760 Torr total pressure. k was determined from the measurement of $COCl_2$ by UV absorption spectroscopy at 240 nm, assumed to be formed in a long chain, involving the reactions Cl + $CHCl_3$ → HCl + CCl_3; $CCl_3 + O_2\ (+M) \rightarrow CCl_3O_2\ (+M)$; $2CCl_3O_2 \rightarrow 2CCl_3O+O_2$; $CCl_3O \rightarrow COCl_2 + Cl$.

(c) Photolysis of CCl_4 in the presence of O_2 with GC or IR analysis of $COCl_2$, formed in 100% yield.

(d) Photolysis of CCl_3CHO in the presence of O_2 with IR analysis of $COCl_2$, formed in 100% yield.

(e) Based on the data of Russell *et al.*[1]

Preferred Values

$k=1.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=8.9\times10^{-14}\exp(860/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–430 K.

$k_2/k=1.0$.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

$\Delta(E/R)=\pm300$ K.

$\Delta(k_2/k)=\pm0.05$.

Comments on Preferred Values

The preferred data are from the study of Russell *et al.*,[1] which is based on the rate of formation of $COCl_2$ from the decomposition reaction $CCl_3O \rightarrow COCl_2 + Cl$, following the interaction of CCl_3O_2 radicals. Additional evidence that the self-reaction of CCl_3O_2 proceeds exclusively through the radical-forming channel [reaction (2)] is derived from the earlier product studies of Jayanty *et al.*[2] and Ohta and Mizoguchi.[3]

References

[1] J. J. Russell, J. A. Seetula, D. Gutman, F. Danis, F. Caralp, P. D. Lightfoot, R. Lesclaux, C. F. Melius, and S. M. Senkan, J. Phys. Chem. **94**, 3277 (1990).

[2] R. K. M. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **4**, 203 (1975).

[3] T. Ohta and I. Mizoguchi, Int. J. Chem. Kinet. **12**, 717 (1980).

[4] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).

$$CH_3CHClO_2 + CH_3CHClO_2 \rightarrow CH_3CHClOH + CH_3COCl + O_2 \quad (1)$$

$$\rightarrow 2CH_3CHClO + O_2 \quad (2)$$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.2\pm1.3)\times10^{-12}$	295	Maricq *et al.*, 1993[1]	(a,b)
Branching Ratios			
$k_2/k=0.95\pm0.05$	295	Maricq *et al.*, 1993[1]	(b)

Comments

(a) k is defined by $-d[CH_3CHClO_2]/dt=2k[CH_3CHClO_2]$.[2]

(b) Pulsed photolysis of Cl_2 in the presence of C_2H_5Cl-O_2-N_2 mixtures with time-resolved IR spectral photography and transient diode laser absorption measurements. The above rate coefficient and branching ratio were obtained from the time-dependence and magnitude of the secondary HCl rise, by computer simulations involving a mechanism of 24 reactions.

Preferred Values

$k_2=5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2/k=0.95$ at 298 K.

Reliability

$\Delta\log k_2=\pm0.3$ at 298 K.

$\Delta(k_2/k)=\pm0.05$ at 298 K.

Comments on Preferred Values

While the data of Maricq *et al.*[1] for the room temperature rate coefficient seem reasonable in relation to the values of other related halogen-containing peroxy radicals, they have been obtained from very indirect measurements. Confirmation by independent measurements is required to lower the recommended error limits.

References

[1] M. M. Maricq, J. Shi, J. J. Szente, L. Rimai, and E. W. Kaiser, J. Phys. Chem. **97**, 9686 (1993).

$$CH_2ClCH_2O_2 + CH_2ClCH_2O_2 \rightarrow CH_2ClCH_2OH + CH_2ClCHO + O_2 \quad (1)$$
$$\rightarrow 2CH_2ClCH_2O + O_2 \quad (2)$$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 1.1\times10^{-13}$ exp(1020/T)	228–380	Dagaut, Wallington, and Kurylo, 1988[1]	(a,b)
$\leq 3.6\times10^{-12}$	298		
$\leq 6.0\times10^{-12}$	295	Maricq *et al.*, 1993[1]	(c)
Branching Ratios			
$k_2/k=0.69$	295	Wallington, Andino, and Japar, 1990[3]	(d)
$k_1/k=0.31$	295		
Reviews and Evaluations			
$k_{obs}=1.1\times10^{-13}$ exp(1020/T)	228–380	Lightfoot *et al.*, 1992[4]	(e)
2.1×10^{-12}	298	Wallington, Dagaut, and Kurylo, 1992[5]	(f)

Comments

(a) k is defined by $-d[CH_2ClCH_2O_2]/dt = 2k[CH_2ClCH_2O_2]^2$ and has been derived from the measured overall second-order decay of $CH_2ClCH_2O_2$ radicals (k_{obs}).

(b) Flash photolysis of Cl_2 in the presence of C_2H_4-O_2-N_2 mixtures over the pressure range 25–400 Torr with UV absorption measurements of $[CH_2ClCH_2O_2]$ using $\sigma_{250} = (3.64\pm0.39)\times10^{-18}$ cm^2 molecule^{-1}. The derived value of k_{obs} is an upper limit to k, because of the possibility of secondary reactions producing an enhanced decay of $CH_2ClCH_2O_2$ radicals (see Comments on Preferred Values).

(c) Pulsed photolysis of Cl_2 in the presence of C_2H_4-O_2-N_2 mixtures at 760 Torr pressure. Time-resolved UV absorption spectra of ($CH_2ClCH_2O_2$ + HO_2). The values of $\sigma(CH_2ClCH_2O_2)$ obtained are ~13% larger than those reported by Dagaut *et al.*[1] [see Comment (b)].

(d) Steady-state photolysis of Cl_2-C_2H_4-O_2-N_2 mixtures at total pressures of 700 Torr with FTIR spectroscopic monitoring of the decay of C_2H_4 and the formation of CH_2ClCHO, CH_2ClCH_2OOH, and CH_2ClCH_2OH. The listed branching ratios were derived from the yields of CH_2ClCH_2OH and CH_2ClCHO relative to the decay of C_2H_4.

(e) Based on the data of Dagaut *et al.*[1]

(f) Calculated from the value $k_{obs}=3.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Dagaut *et al.*[1]) and $k_2/k=0.69$ (Wallington *et al.*[3]) at 295 K.

Preferred Values

$k \leq 4.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k \leq 1.6\times10^{-13}$ exp(1020/T) cm^3 molecule^{-1} s^{-1} over the temperature range 220–380 K.

$k_2/k=0.7$ at 298 K.

Reliability

$\Delta(k_2/k) = \pm0.1$ at 298 K.

Comments on Preferred Values

The upper limits to the overall rate coefficient from the studies of Dagaut *et al.*[1] and Maricq *et al.*[2] differ by 67%. A small part of this discrepancy is accounted for by the different absorption cross sections for the $CH_2ClCH_2O_2$ radical observed by these authors, but a large part of the difference is still unresolved. In addition, there is the difficulty of correcting the observed rate coefficients of the second-order decay of $CH_2ClCH_2O_2$ radicals for the secondary chemistry. The rate coefficient for the self-reaction of $CH_2ClCH_2O_2$ radicals is quite large and it is not certain that the rate of the reaction HO_2 + $CH_2ClCH_2O_2$ will be large enough to compete with the self-reaction of $CH_2ClCH_2O_2$ radicals.

We have averaged the results of Dagaut *et al.*[1] and Maricq *et al.*[2] to obtain an upper limit of the overall rate coefficient at 298 K. This value was then used to adjust the *A*-factor from the temperature-dependent data of Dagaut *et al.*[1] to obtain the recommended Arrhenius equation.

References

[1] P. Dagaut, T. J. Wallington, and M. J. Kurylo, Chem. Phys. Lett. **146**, 589 (1988).

[2] M. M. Maricq, J. Shi, J. J. Szente, L. Rimai, and E. W. Kaiser, J. Phys. Chem. **97**, 9686 (1993).

[3] T. J. Wallington, J. M. Andino, and S. M. Japar, Chem. Phys. Lett. **165**, 189 (1990).

[4] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).

[5] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).

$O_3 + C_2HCl_3 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k < 5 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The upper limit to the preferred value is taken from the data of Atkinson *et al.*,[1] with the upper limit being increased by a factor of ~2 to take into account additional uncertainties in the study of Atkinson *et al.*[1] This upper limit is consistent with the reported data for the reactions of O_3 with the chloroethenes,[2] which show that Cl atom substitution markedly decreases the rate coefficients at room temperature, relative to that for ethene. The preferred value is identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] R. Atkinson, S. M. Aschmann, D. R. Fitz, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **14**, 13 (1982).

[2] R. Atkinson and W. P. L. Carter, Chem. Rev. **84**, 437 (1984).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O_3 + C_2Cl_4 \rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$k < 10^{-21}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The upper limit to the preferred value is derived from the very limited amount of data reported by Mathias *et al.*,[1] with the upper limit to the rate coefficient being increased by a factor of 50 over that reported. This upper limit to the rate coefficient for C_2Cl_4 is consistent with the kinetic data for the other chloroethenes,[2] which show that Cl atom substitution markedly decreases the reactivity of the chloroethenes towards O_3, compared to that for ethene. The preferred value is identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] E. Mathias, E. Sanhueza, I. C. Hisatsune, and J. Heicklen, Can. J. Chem. **52**, 3852 (1974).

[2] R. Atkinson and W. P. L. Carter, Chem. Rev. **84**, 437 (1984).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

HCl + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
HCl + $h\nu \rightarrow$ H + Cl	432	277

Preferred Values

Absorption cross-sections for HCl photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
140	211	180	58.8
145	281	185	31.3
150	345	190	14.5
155	382	195	6.18
160	332	200	2.56
165	248	205	0.983
170	163	210	0.395
175	109	215	0.137
		220	0.048

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are those reported by Inn.[1] Photolysis is expected to occur with unit quantum efficiency. The preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] E. C. Y. Inn, J. Atmos. Sci. **32**, 2375 (1975).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

HOCl + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$HOCl + h\nu \rightarrow HO + Cl$ (1)	239	500
$\rightarrow HCl + O(^3P)$ (2)	235	510

Preferred Values

Absorption cross-sections for HOCl photolysis at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
200	7.1	295	5.7
205	5.5	300	6.0
210	5.7	305	6.0
215	7.0	310	5.9
220	9.7	315	5.5
225	12.8	320	4.9
230	16.4	325	4.2
235	19.2	330	3.5
240	20.7	335	2.9
245	20.0	340	2.4
250	17.3	345	1.8
255	13.9	350	1.5
260	10.5	355	1.2
265	7.8	360	0.8
270	6.0	365	0.9
275	5.0	370	0.8
280	4.7	375	0.8
285	4.8	380	0.8
290	5.3		

Quantum Yield for HOCl Photolysis at 298 K

$\phi_1 = 1.0$ for $\lambda > 200$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported recently by Burkholder[1] (where values are tabulated at 2 nm intervals). They differ significantly from our previous recommendation (IUPAC, 1992[2]) which was based on the results of Permien *et al.*[3] Earlier results are discussed in IUPAC, 1989.[4] Discrepancies between studies arise in correcting for spectral interference from Cl_2O and Cl_2. The preferred quantum yield values are based on the results of Molina *et al.*,[5] Butler and Phillips,[6] and Vogt and Schindler.[7]

References

[1] J. B. Burkholder, J. Geophys. Res. **98**, 2963 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] T. Permien, R. Vogt, and R. N. Schindler, in *Mechanisms of Gas Phase and Liquid Phase Chemical Transformations in Tropospheric Chemistry*, edited by R. A. Cox, Air Pollution Research Report No. 17, Environmental Research Program of the CEC, EUR 12035 EN, Brussels, Belgium.

[4] IUPAC, Supplement III, 1989 (see references in Introduction).

[5] M. J. Molina, T. Ishiwata, and L. T. Molina, J. Phys. Chem. **84**, 821 (1980).

[6] P. J. D. Butler and L. F. Phillips, J. Phys. Chem. **87**, 183 (1983).

[7] R. Vogt and R. N. Schindler, J. Photochem. Photobiol. A: Chem. **66**, 133 (1992).

OClO + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
OClO + $h\nu \rightarrow$ ClO + O(^{3}P)	(1)	255	470
$\rightarrow$ Cl + O_2	(2)	26	4700

Preferred Values

Absorption cross-sections of OClO at the band peaks at 204 K, 296 K, and 378 K

	$10^{20}\sigma$/cm^2		
λ/nm	204 K	296 K	378 K
475.53	-	13	-
461.15	17	17	16
446.41	94	69	57
432.81	220	166	134
420.58	393	304	250
408.83	578	479	378
397.76	821	670	547
387.37	1046	844	698
377.44	1212	992	808
368.30	1365	1136	920
359.73	1454	1219	984
351.30	1531	1275	989
343.44	1507	1230	938
336.08	1441	1139	864
329.22	1243	974	746
322.78	1009	791	628
317.21	771	618	516
311.53	542	435	390
305.99	393	312	291
300.87	256	219	216
296.42	190	160	167
291.77	138	114	130
287.80	105	86	105
283.51	89	72	90
279.64	73	60	79
275.74	59	46	-
272.93	53	33	-

Quantum Yields for OClO Photolysis at 298 K

$\phi_1 = 1.0$ throughout the wavelength range 270–480 nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at the peak of the bands [a(0) to a(26)] at 204 K, 296 K, and 378 K are the values reported by Wahner *et al.*[1] The bands became appreciably sharper with decreasing temperature.[1] However, the integrated band intensities remained constant for all bands between 204 K and 296 K, and therefore the solar photolysis rate is not expected to have a significant temperature dependence. The recommended quantum yield of unity for O-atom production is based on results reported by Colussi,[2] and results of earlier studies discussed in the review by Watson.[3] Colussi,[2] in a laser flash photolysis study at 308 nm, determined the quantum yield for O atom production to be 1.02±0.05 and the quantum yield for Cl atom production to be <0.01. Vaida and co-workers[4,5] reported the detection of Cl atoms by resonance-enhanced multiphoton ionization (REMPI) in the photodecomposition of OClO in the region 360–363 nm. They interpreted this as resulting from the photoisomerization of OClO to ClOO followed by dissociation to Cl + O_2, but did not report quantum yields. Bishenden *et al.*,[6] using REMPI detection of Cl atoms, report that the quantum yield for Cl atom formation near 360 nm is 0.15±0.10. In contrast, Lawrence *et al.*,[7] using a technique involving charge transfer excitation of Cl-Xe collision pairs as a sensitive probe of Cl atoms, determined that the quantum yield for Cl atom production in the 359–368 nm region is $<5\times10^{-4}$. In a molecular beam photofragment study over the wavelength range 350–475 nm, Davis and Lee[8] observed the dominant products to be ClO + O and also observed Cl atom yields reaching a maximum of 3.9% near 404 nm, decreasing to <0.2% in the wavelength range 350–370 nm, in qualitative agreement with the results of Lawrence *et al.*[7]

References

[1] A. Wahner, G. S. Tyndall, and A. R. Ravishankara, J. Phys. Chem. **91**, 2734 (1987).

[2] A. J. Colussi, J. Phys. Chem. **94**, 8922 (1990).

[3] R. T. Watson, J. Phys. Chem. Ref. Data **6**, 871 (1977).

[4] V. Vaida, S. Solomon, E. C. Richard, E. Ruhl, and A. Jefferson, Nature **342**, 405 (1989).

[5] E. Ruhl, A. Jefferson, and V. Vaida, J. Phys. Chem. **94**, 2990 (1990).

[6] E. Bishenden, J. Haddock, and D. J. Donaldson, J. Phys. Chem. **95**, 2113 (1991); J. Phys. Chem. **96**, 6513 (1992).

[7] W. G. Lawrence, K. C. Clemitshaw, and V. A. Apkarian, J. Geophys. Res. **95**, 18591 (1990).

[8] H. F. Davis and Y. T. Lee, J. Phys. Chem. **96**, 5681 (1992).

$Cl_2O + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$Cl_2O + h\nu \rightarrow Cl + ClO$	(1)	142	840
$\rightarrow O + Cl_2$	(2)	168	710
$\rightarrow O + 2\,Cl$	(3)	410	292

Preferred Values

Absorption cross-sections for Cl_2O photolysis at 298 K

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2
200	71.0	330	8.40
210	23.8	340	3.58
220	8.6	350	1.54
230	28.1	360	0.73
240	103	370	0.40
250	191	380	0.36
260	195	390	0.51
270	151	400	0.79
280	126	420	1.26
290	103	440	1.11
300	71.0	460	0.63
310	40.3	480	0.32
320	19.5	500	0.22

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Knauth *et al.*[1] and are identical to our previous evaluation, IUPAC, 1992.[2] The preferred values are in excellent agreement with the values reported by Molina and Molina,[3] except for the 330–400 nm range where the values in Ref. 3 are higher, and they are in reasonable agreement with the values reported by Lin.[4] Values for the 150–200 nm wavelength region have recently been reported by Nee.[5]

Photolysis proceeds predominantly by breaking of the Cl-O bond to yield Cl + ClO. However, in the most recent study of the products of Cl_2O photolysis, Sander and Friedl[6] determined the quantum yield for formation of oxygen atoms from Cl_2O photolysis to be 0.25 ± 0.05. In these experiments a broad-band photolysis source with a spectral distribution extending from the visible down to 180 nm was used, so that it was not possible to determine the wavelength dependence of the quantum yield.

References

[1] H. D. Knauth, H. Alberti, and H. Clausen, J. Phys. Chem. **83**, 1604 (1979).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] L. T. Molina and M. J. Molina, J. Phys. Chem. **82**, 2410 (1978).

[4] C. L. Lin, J. Chem. Eng. Data **21**, 411 (1976).

[5] J. B. Nee, J. Quant. Spectrosc. Radiat. Transfer **46**, 55 (1991).

[6] S. P. Sander and R. R. Friedl, J. Phys. Chem. **93**, 4764 (1989).

$Cl_2O_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$Cl_2O_2 + h\nu \rightarrow ClO + ClO$	(1)	76	1580
$\rightarrow Cl + ClOO$	(2)	91	1310

Preferred Values

Absorption cross-sections for Cl_2O_2 photolysis at 200–250 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	383.5	250	609.3	300	72.2	350	8.2
2	352.9	2	580.1	2	65.8	2	7.9
4	325.3	4	544.5	4	59.9	4	6.8
6	298.6	6	505.4	6	54.1	6	6.1
8	274.6	8	631.5	8	79.0	8	5.8
210	251.3	260	422.0	310	43.3	360	5.5
2	231.7	2	381.4	2	38.5	2	4.5
4	217.0	4	344.6	4	34.6	4	4.1
6	207.6	6	311.6	6	30.7	6	3.8
8	206.1	8	283.3	8	28.0	8	3.5
220	212.1	270	258.4	320	25.6	370	3.2
2	227.1	2	237.3	2	23.4	2	2.9
4	249.4	4	218.3	4	21.4	4	2.7
6	280.2	6	201.6	6	19.2	6	2.4
8	319.5	8	186.4	8	17.8	8	2.2
230	365.0	280	172.5	330	16.7	380	2.1
2	415.4	2	159.6	2	15.6	2	1.9
4	467.5	4	147.3	4	14.4	4	1.7
6	517.5	6	136.1	6	13.3	6	1.6
8	563.0	8	125.2	8	13.1	8	1.4
240	600.3	290	114.6	340	12.1	390	1.3
2	625.7	2	104.6	2	11.5	2	1.2
4	639.4	4	95.4	4	10.9	4	1.1
6	642.6	6	87.1	6	10.1	6	1.0
8	631.5	8	79.0	8	9.0	8	0.9

Quantum Yields

$\phi_2 = 1.0$ throughout this wavelength range.

Comments on Preferred Values

The preferred values of the absorption cross-sections given here are the values recommended in the NASA, 1994 evaluation.[1] For the wavelength range 200–360 nm they are the smoothed average of the results reported by Cox and Hayman,[2] DeMore and Tschuikow-Roux,[3] Permien *et al.*,[4] and Burkholder *et al.*;[5] for wavelengths greater than 360 nm the values were derived from a linear extrapolation of log $\sigma(\lambda)$ vs λ using the expression: $\log(10^{20}\sigma/\text{cm}^2) = (7.589 - 0.01915\ \lambda)$. These studies indicate that in the recombination reaction ClO + ClO → products, the only stable species produced is ClOOCl. The structure of the recombination product has been established to be ClOOCl by the study of Birk *et al.*[6] using submillimeter wave spectroscopy. Theoretical studies[7–9] of thermochemical stabilities of Cl_2O_2 isomers are in agreement with these observations. The preferred quantum yield values are based on results of the study by Molina *et al.*[10] in which the production of Cl atoms in the laser flash photolysis of ClOOCl at 308 nm was directly determined by time-resolved atomic resonance fluorescence. These results are in agreement with the interpretation of the steady-state photolysis experiments of Cox and Hayman.[2]

References

[1] NASA Evaluation No. 11, 1994 (see references in Introduction).

[2] R. A. Cox and G. D. Hayman, Nature **332**, 796 (1988).

[3] W. B. DeMore and E. Tschuikow-Roux, J. Phys. Chem. **94**, 5856 (1990).

[4] T. Permien, R. Vogt, and R. N. Schindler, in *Mechanisms of Gas Phase and Liquid Phase Chemical Transformations in Tropospheric Chemistry*, edited by R. A. Cox, Air Pollution Research No. 17, Environmental Research Program of the CEC, EUR 12035 EN, Brussels, Belgium.

[5] J. B. Burkholder, J. J. Orlando, and C. J. Howard, J. Phys. Chem. **94**, 687 (1990).

[6] M. Birk, R. Friedl, E. Cohen, H. Pickett, and S. P. Sander, J. Chem. Phys. **91**, 6588 (1989).

[7] M. P. McGrath, K. C. Clemitshaw, F. S. Rowland, and W. J. Hehre, J. Phys. Chem. **94**, 6126 (1990); Geophys. Res. Lett. **15**, 883 (1988).

[8] F. Jensen and J. Oddershede, J. Phys. Chem. **94**, 2235 (1990).

[9] J. F. Stanton, C. M. L. Rittby, R. J. Bartlett, and D. W. Toohey, J. Phys. Chem. **95**, 2107 (1991); J. F. Stanton and R. J. Bartlett, J. Chem. Phys. **98**, 9335 (1993).

[10] M. J. Molina, A. J. Colussi, L. T. Molina, R. N. Schlindler, and T. L. Tso, Chem. Phys. Lett. **173**, 310 (1990).

$Cl_2O_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$Cl_2O_3 + h\nu \rightarrow ClO + OClO$ (1)	44	2720
$\rightarrow Cl + ClO_3$ (2)	201	595

Preferred Values

Absorption cross-sections for Cl_2O_3 photolysis at 200–260 K

λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$
220	968	280	1136
225	930	285	890
230	908	290	642
235	883	295	435
240	904	300	288
245	989	305	176
250	1154	310	107
255	1352	315	56
260	1512	320	36
265	1594		
270	1544		
275	1376		

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Burkholder *et al.*[1] They show no dependence on temperature over the range 200–260 K. The results of this more direct study[1] are preferred over those of Hayman and Cox,[2] which formed the basis for our previous recommendation.[3] These two studies[1,2] are in agreement on the shape of the spectrum, but the values reported by Hayman and Cox[2] are approximately 30–50% larger. The mechanism and quantum yield for photodissociation have not been determined.

References

[1] J. B. Burkholder, R. L. Mauldin, R. J. Yokelson, S. Solomon, and A. R. Ravishankara, J. Phys. Chem. **97**, 7597 (1993).

[2] G. D. Hayman and R. A. Cox, Chem. Phys. Lett. **155**, 1 (1989).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

ClNO + $h\nu$ → products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
ClNO + $h\nu$ → Cl + NO	160	750

Preferred Values

Absorption cross-sections for ClNO photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	4320	246	45.2	302	10.3	370	11.0
192	5340	248	37.7	304	10.5	375	9.95
194	6150	250	31.7	306	10.8	380	8.86
196	6480	252	27.4	308	11.1	385	7.82
198	6310	254	23.7	310	11.5	390	6.86
200	5860	256	21.3	312	11.9	395	5.97
202	5250	258	19.0	314	12.2	400	5.13
204	4540	260	17.5	316	12.5	405	4.40
206	3840	262	16.5	318	13.0	410	3.83
208	3210	264	15.3	320	13.4	415	3.38
210	2630	266	14.4	322	13.6	420	2.89
212	2180	268	13.6	324	14.0	425	2.45
214	1760	270	12.9	326	14.3	430	2.21
216	1400	272	12.3	328	14.6	435	2.20
218	1110	274	11.8	330	14.7	440	2.20
220	896	276	11.3	332	14.9	445	2.07
222	707	278	10.7	334	15.1	450	1.87
224	552	280	10.6	336	15.3	455	1.79
226	436	282	10.2	338	15.3	460	1.95
228	339	284	9.99	340	15.2	465	2.25
230	266	286	9.84	342	15.3	470	2.50
232	212	288	9.71	344	15.1	475	2.61
234	164	290	9.64	346	15.1	480	2.53
236	128	292	9.63	348	14.9	485	2.33
238	101	294	9.69	350	14.5	490	2.07
240	82.5	296	9.71	355	13.6	495	1.78
242	67.2	298	9.89	360	12.9	500	1.50
244	55.1	300	10.0	365	12.0		

Quantum Yields for ClNO Photolysis at 298 K

$\phi = 1.0$ over the entire wavelength range.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K for the wavelength range 190–350 nm (unchanged from IUPAC, 1992[1]) are the values reported by Tyndall *et al.*[2] and for the longer wavelengths are the values reported in the recent study of Roehl *et al.*[3] Roehl *et al.*[3] reported values over the wavelength range 350–650 nm and the temperature range 223–343 K. Earlier results are discussed in NASA, 1994.[4] The preferred quantum yield values are taken from Calvert and Pitts.[5]

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).

[2] G. S. Tyndall, K. M. Stedman, W. Schneider, J. P. Burrows, and G. K. Moortgat, J. Photochem. **36**, 133 (1987).

[3] C. M. Roehl, J. J. Orlando, and J. G. Calvert, J. Photochem. Photobiol. A: Chem. **69**, 1 (1992).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

[5] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966), p. 230.

$ClONO + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$ClONO + h\nu \rightarrow Cl + NO_2$ (1)	98	1220
$\rightarrow ClO + NO$ (2)	136	880

Preferred Values

Absorption cross-sections for ClONO photolysis at 231 K

λ/nm	$10^{20}\ \sigma/cm^2$	λ/nm	$10^{20}\ \sigma/cm^2$
235	215.0	320	80.3
240	176.0	325	75.4
245	137.0	330	58.7
250	106.0	335	57.7
255	65.0	340	43.7
260	64.6	345	35.7
265	69.3	350	26.9
270	90.3	355	22.9
275	110.0	360	16.1
280	132.0	365	11.3
285	144.0	370	9.0
290	144.0	375	6.9
295	142.0	380	4.1
300	129.0	385	3.3
305	114.0	390	2.2
310	105.0	395	1.5
315	98.1	400	0.6

Comments on Preferred Values

The preferred values of the absorption cross-sections at 231 K are the values reported by Molina and Molina.[1] Photolysis is expected to occur with unit quantum efficiency by breaking of the Cl-O bond to yield $Cl + NO_2$. The lifetime against photodissociation for ClONO in the atmosphere was calculated to 2 to 3 minutes.[1] The preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] L. T. Molina and M. J. Molina, Geophys. Res. Lett. **4**, 83 (1977).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$ClNO_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$ClNO_2 + h\nu \rightarrow Cl + NO_2$ (1)	142	840
$\rightarrow ClNO + O(^3P)$ (2)	288	415

Preferred Values

Absorption cross-sections for $ClNO_2$ photolysis at 298 K

λ/nm	$10^{20}\ \sigma/cm^2$	λ/nm	$10^{20}\ \sigma/cm^2$
190	2690	290	17.3
200	468	300	14.9
210	320	310	12.1
220	339	320	8.87
230	226	330	5.84
240	133	340	3.54
250	90.6	350	2.04
260	61.3	360	1.15
270	35.3	370	0.69
280	22.0		

Comments on Preferred Values

The preferred values of the absorption cross-sections are the values reported in the recent study of Ganske *et al.*[1] They are in good agreement with our previous recommendation,[2] which for 190–270 nm were the values reported by Illies and Takacs,[3] and for 270–370 nm were the values reported by Nelson and Johnston.[4] The latter authors[4] showed that the higher values above 300 nm reported in Ref. 3 could be accounted for by a 6% Cl_2 impurity in the $ClNO_2$ sample. Nelson and Johnston[4] determined that photolysis occurs with a quantum yield of unity (within experimental error) to produce $Cl + NO_2$ ($\phi_1 = 0.93 \pm 0.15$). They also reported a negligible production of oxygen atoms ($\phi_2 < 0.02$).

References

[1] J. A. Ganske, H. N. Berko, and B. J. Finlayson-Pitts, J. Geophys. Res. **97**, 7651 (1992).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] A. J. Illies and G. A. Takacs, J. Photochem. **6**, 35 (1976/77).
[4] H. H. Nelson and H. S. Johnston, J. Phys. Chem. **85**, 3891 (1981).

$ClONO_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$ClONO_2 + h\nu \rightarrow ClO + NO_2$	(1)	112	1065
$\rightarrow Cl + NO_3$	(2)	163	735
$\rightarrow ClONO + O(^3P)$	(3)	282	425

Preferred Values

Absorption cross-sections for $ClONO_2$ photolysis at 296 K, 220 K

	10^{20} σ/cm^2			10^{20} σ/cm^2	
λ/nm	296 K	220 K	λ/nm	296 K	220 K
200	282	270	315	1.14	
205	284		320	0.831	0.578
210	314	315	325	0.613	
215	342		330	0.466	0.329
220	332	335	335	0.367	
225	278		340	0.302	0.230
230	208	200	345	0.258	
235	148		350	0.229	0.186
240	105	96.7	355	0.208	
245	76.4		360	0.200	0.169
250	56.0	49.7	365	0.180	
255	43.2		370	0.159	0.136
260	33.8	29.1	375	0.141	
265	26.5		380	0.121	0.104
270	20.5	17.3	385	0.137	
275	15.7		390	0.091	0.077
280	11.9	9.83	395	0.076	
285	8.80		400	0.064	0.052
290	6.41	5.15	405	0.054	
295	4.38		410	0.044	0.034
300	3.13	2.40	415	0.036	
305	2.24		420	0.032	0.023
310	1.60	1.16	425	0.023	
			430	0.019	0.013

Quantum Yields for $ClONO_2$ Photolysis

$\phi_2=0.90$ for $\lambda>260$ nm.
$\phi_3=0.10$ for $\lambda>260$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections are taken from Burkholder *et al.*,[1] who measured values over the wavelength range 195–430 nm and the temperature range 220–296 K. They report,[1] every 2 nm, values of σ at 296 K and values of the parameters A_1 and A_2 needed to compute the temperature dependence by the equation:

$$\sigma(\lambda,T)/\sigma(\lambda,296)=1+A_1(T-296)+A_2(T-296)^2.$$

In this data sheet, room temperature values at 5 nm intervals are given (odd wavelength values were calculated by linear interpolation) and, at 10 nm intervals, 220 K values calculated using the formula shown above and the parameters tabulated in the paper. For values of σ at every 2 nm and values of the temperature dependence parameters, the reader is referred to the original reference.[1] These values are in good agreement with those reported in IUPAC, 1992,[2] which were based on the results of Molina and Molina.[3] The preferred quantum yield values are based on the direct results of Margitan[4] at 266 nm and 355 nm. They are confirmed by the results of Knauth and Schindler[5] based on final product analysis, and also by the results of Chang *et al.*[6] and Burrows *et al.*,[7] who report Cl + NO_3 as the photolysis products at 254 nm, with a quantum yield of unity. However, in contrast with these results, in a recent study using a molecular beam technique with pulsed laser photolysis, Minton *et al.*[8] report comparable values of ϕ_1 and ϕ_2 at 193 nm and 248 nm.

References

[1] J. B. Burkholder, R. K. Talukdar, and A. R. Ravishankara, Geophys. Res. Lett. **21**, 585 (1994).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] L. T. Molina and M. J. Molina, J. Photochem. **11**, 139 (1979).
[4] J. J. Margitan, J. Phys. Chem. **87**, 674 (1983).
[5] H. D. Knauth and R. N. Schindler, Z. Naturforsch. Teil A **38**, 393 (1983).
[6] J. S. Chang, J. R. Barker, J. E. Davenport, and D. M. Golden, Chem. Phys. Lett. **60**, 385 (1979).
[7] J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, J. Phys. Chem. **92**, 4340 (1988).
[8] T. K. Minton, C. M. Nelson, T. A. Moore, and M. Okumura, Science **258**, 1342 (1992).

$Cl_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$Cl_2 + h\nu \rightarrow Cl + Cl$	242	495

Preferred Values

Absorption cross-sections for Cl_2 photolysis at 298 K

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2
260	0.20	370	8.4
270	0.82	380	5.0
280	2.6	390	2.9
290	6.2	400	1.8
300	11.9	410	1.3
310	18.5	420	0.96
320	23.7	430	0.73
330	25.5	440	0.54
340	23.5	450	0.38
350	18.8	460	0.26
360	13.2	470	0.16

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported in the recent study of Maric *et al.*[1] The results of the recent study of Ganske *et al.*[2] are in excellent agreement. Results of these two studies[1,2] are in good agreement with the previous recommendation (IUPAC, 1992[3]) which was based on the study of Seery and Britton.[4] Additional earlier studies are cited in IUPAC, 1992.[3] Maric *et al.*[1] fitted the data for the wavelength region 250–550 nm with the following semiempirical expression:

$$10^{20}\sigma = \alpha^{0.5} \times 27.3\ \exp\{-99.0\alpha[\ln(329.5/\lambda)]^2\} + \alpha^{0.5} \times 0.932\ \exp\{-91.5\alpha[\ln(406.5/\lambda)\}^2\}$$

where $\alpha = \tanh(402.676/T)$.

This expression combines the semiempirical function originally proposed by Johnston *et al.*[5] with the temperature dependence expressions proposed by Sulzer and Wieland.[6]

References

[1] D. Maric, J. P. Burrows, R. Meller, and G. K. Moortgat, J. Photochem. Photobiol. A: Chem. **70**, 205 (1993).

[2] J. A. Ganske, H. N. Berko, and B. J. Finlayson-Pitts, J. Geophys. Res. **97**, 7651 (1992).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] D. J. Seery and D. Britton, J. Phys. Chem. **68**, 2263 (1964).

[5] H. S. Johnston, M. Paige, and F. Yao, J. Geophys. Res. **89**, 11661 (1984).

[6] P. Sulzer and K. Wieland, Helv. Phys. Acta. **25**, 653 (1952).

CH_3Cl + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3Cl + h\nu \rightarrow CH_3 + Cl$	349	343

Preferred Values

Absorption cross-sections for CH_3Cl photolysis at 295 K and 210 K

	10^{20} σ/cm^2			10^{20} σ/cm^2	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
174	111	111	200	1.76	1.51
6	93.8	93.8	2	1.13	0.93
8	76.6	76.6	4	0.750	0.573
180	60.7	60.7	6	0.483	0.345
2	46.7	46.7	8	0.318	0.212
4	35.0	35.0	210	0.206	0.130
6	25.5	25.5	2	0.132	0.080
8	18.2	18.2	4	0.086	0.047
190	12.7	12.7	6	0.055	0.027
2	8.72	8.72			
4	5.88	5.88			
6	4.01	4.01			
8	2.66	2.43			

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K and at 210 K are the values reported to Simon *et al.*[1] and are identical to our previous evaluation, IUPAC, 1992.[2] This publication[1] reports the results of the most comprehensive study of the temperature dependence. These values are in very good agreement with the room temperature values reported by Robbins,[3] and are in reasonable agreement with the results of Hubrich *et al.*[4] who also made low temperature measurements. In this wavelength region, photolysis occurs with unit quantum efficiency by breaking of the C-Cl bond to yield CH_3 + Cl. Photochemistry at shorter wavelengths is discussed by Shold and Rebbert.[5]

References

[1] P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, J. Atmos. Chem. **7**, 107 (1988).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] D. E. Robbins, Geophys. Res. Lett. **3**, 213 (1976); erratum op. cit. **3**, 757 (1976).
[4] C. Hubrich, C. Zetzsch, and F. Stuhl, Ber. Bunsenges. Phys. Chem. **81**, 437 (1977).
[5] D. M. Shold and R. E. Rebbert, J. Photochem. **9**, 499 (1978).

CHF_2Cl(HCFC-22) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CHF_2Cl + h\nu \rightarrow CHF_2 + Cl$	362	330

Preferred Values

Absorption cross-sections for CHF_2Cl photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
174	5.72	190	0.245
176	4.04	192	0.156
178	2.76	194	0.103
180	1.91	196	0.072
182	1.28	198	0.048
184	0.842	200	0.032
186	0.576	202	0.022
188	0.372	204	0.014

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Simon *et al.*[1] and are identical to our previous evaluation, IUPAC, 1992.[2] In the same study[1] the temperature dependence down to 210 K has been reported, with the values at the shorter wavelengths being temperature-independent while the values at longer wavelengths show a decrease as the temperature is lowered.[1] For values at low temperatures the reader is referred to the original reference. These results are in reasonable agreement with the results of earlier studies cited in NASA, 1990.[3] Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CHF_2 + Cl.

References

[1] P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, J. Atmos. Chem. **7**, 107 (1988).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 9, 1990 (see references in Introduction).

CF_2Cl_2(CFC-12) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$ (1)	346	346
$\rightarrow CF_2 + 2\,Cl$ (2)	542	221

Preferred Values

Absorption cross-sections for CF_2Cl_2 photolysis at 295 K and 210 K

	$10^{20}\ \sigma/cm^2$			$10^{20}\ \sigma/cm^2$	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
174	162	162	200	8.89	5.11
6	181	181	2	5.51	2.97
8	187	187	4	3.44	1.69
180	179	179	6	2.09	0.99
2	160	160	8	1.27	0.56
4	134	134	210	0.76	0.32
6	107	107	2	0.45	0.18
8	82.8	79.3	4	0.27	0.10
190	63.2	52.9	6	0.16	0.058
2	45.4	35.8	8	0.10	0.033
4	31.5	22.8	220	0.060	0.018
6	21.1	14.4	2	0.036	0.010
8	13.9	8.8	4	0.022	0.006
			6	0.013	0.003

Quantum yields for CF_2Cl_2 photolysis at 298 K

λ/nm	ϕ_1	ϕ_2	λ/nm	ϕ_1	ϕ_2
170	0.59	0.41	210	0.85	0.15
180	0.62	0.38	220	0.96	0.04
190	0.67	0.33	230	1.0	
200	0.74	0.26	240	1.0	

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K and at 210 K are the values reported by Simon *et al.*[1] This recent publication reports the results of the most comprehensive study of the temperature dependence.[1] The values at room temperature are in good agreement with those recommended in our previous evaluation, CODATA, 1980,[2] where a detailed discussion of earlier work can be found. The recommended quantum yield values are taken from Ref. 2, and are based on the results of Rebbert and Ausloos.[3] The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, J. Atmos. Chem. **7**, 107 (1988).
[2] CODATA, 1980 (see references in Introduction).
[3] R. E. Rebbert and P. J. Ausloos, J. Photochem. **4**, 419 (1975).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CFCl_3$(CFC-11) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$ (1)	317	380
$\rightarrow CFCl + 2\,Cl$ (2)	507	236

Preferred Values

Absorption cross-sections for $CFCl_3$ photolysis at 295 K and 210 K

	10^{20} σ/cm^2			10^{20} σ/cm^2	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
174	313	313	210	14.8	9.9
6	324	324	2	10.5	6.63
8	323	323	4	7.56	4.31
180	314	414	6	5.38	2.78
2	296	296	8	3.79	1.77
4	272	272	220	2.64	1.13
6	243	230	2	1.82	0.71
8	213	202	4	1.24	0.45
190	179	170	6	0.84	0.29
2	154	141	8	0.56	0.19
4	124	115	230	0.37	0.12
6	99.1	90.5	235	0.126	
8	78.0	71.8	240	0.046	
200	64.5	55.8	245	0.017	
2	50.0	42.0	250	0.0066	
4	37.4	30.0	255	0.0034	
6	28.0	21.6	260	0.0015	
8	19.7	14.9			

Quantum yields for $CFCl_3$ photolysis at 298 K

λ/nm	ϕ_1	ϕ_2	λ/nm	ϕ_1	ϕ_2
170	0.57	0.43	210	0.84	0.16
180	0.66	0.34	220	0.94	0.06
190	0.66	0.34	230	1.0	
200	0.74	0.26	240	1.0	

Comments on Preferred Values

The preferred values of the absorption cross-sections for 174–230 nm at 295 K and 210 K are the values reported by Simon *et al.*[1] This recent publication reports the results of the most comprehensive study of the temperature dependence.[1] The values are in good agreement with those recommended in our previous evaluation, CODATA, 1982,[2] where a detailed discussion of earlier work can be found. For λ>230 nm, the absorption cross-section values are those reported by Hubrich and Stuhl.[3] The recommended quantum yield values are taken from Ref. 2, and are based on the results of Rebbert and Ausloos.[4] The preferred values are identical to our previous evaluation, IUPAC, 1992.[5]

References

[1] P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, J. Atmos. Chem. **7**, 107 (1988).

[2] CODATA, Supplement I, 1982 (see references in Introduction).

[3] C. Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).

[4] R. E. Rebbert and P. J. Ausloos, J. Photochem. **4**, 419 (1975).

[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CCl_4 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CCl_4 + h\nu \rightarrow CCl_3 + Cl$ (1)	288	415
$\rightarrow CCl_2 + 2\,Cl$ (2)	577	207

Preferred Values

Absorption cross-sections for CCl_4 photolysis at 295 K and 210 K

	10^{20} σ/cm^2			10^{20} σ/cm^2	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
174	990	990	220	17.5	12.5
6	1010	1010	2	13.6	9.0
8	975	975	4	10.2	6.4
180	720	720	6	7.6	4.4
2	590	590	8	5.6	3.16
4	440	440	230	4.28	2.27
6	310	310	2	3.04	1.52
8	198	198	4	2.20	1.05
190	147	147	6	1.60	0.72
2	99.2	99.2	8	1.16	0.50
4	76.7	76.7	240	0.830	0.342
6	69.5	69.5	2	0.590	0.234
8	68.0	68.0	4	0.413	0.158
200	66.0	66.0	6	0.290	0.108
2	63.8	63.8	8	0.210	0.076
4	61.0	60.1	250	0.148	0.053
6	57.0	54.4	255	0.066	
8	52.5	48.3	260	0.025	
210	46.9	41.5	265	0.013	
2	41.0	34.8	270	0.006	
4	34.5	27.9	275	0.002	
6	27.8	21.7			
8	22.1	16.3			

Quantum yields for CCl_4 photolysis at 298 K

λ/nm	ϕ_1	ϕ_2	λ/nm	ϕ_1	ϕ_2
170	0.30	0.70	210	0.83	0.17
180	0.36	0.64	220	0.96	0.04
190	0.46	0.54	230	1.0	
200	0.63	0.37	240	1.0	

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K and 210 K are the values reported by Simon *et al.*[1] This recent publication reports the results of the most comprehensive study of the temperature dependence.[1] The values at room temperature are in good agreement with those recommended in our previous evaluation, CODATA, 1982,[2] where a detailed discussion of earlier work can be found. For λ>250 nm, the absorption cross-section values are those reported by Hubrich and Stuhl.[3] The recommended quantum yield values are taken from Ref. 2, and are based on the results of Rebbert and Ausloos.[4] The preferred values are identical to our previous evaluation, IUPAC, 1992.[5]

References

[1] P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, J. Atmos. Chem. **7**, 107 (1988).
[2] CODATA, Supplement I, 1982 (see references in Introduction).
[3] C. Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).
[4] R. E. Rebbert and P. J. Ausloos, J. Photochem. **6**, 265 (1976/77).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

CH_3CF_2Cl(HCFC-142b) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CF_2Cl + h\nu \rightarrow CH_3CF_2 + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for CH_3CF_2Cl photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	0.94	210	0.017
2	0.66	2	0.010
4	0.46	4	0.007
6	0.31	6	0.004
8	0.21	8	0.003
200	0.14	220	0.002
2	0.09	2	0.0009
4	0.061	4	0.0005
6	0.039	6	0.0003
8	0.026	8	0.0002

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon[1] and Orlando *et al.*[2] The agreement between these studies[1,2] over the wavelength range of preferred values is good. The results of Hubrich and Stuhl[3] are in reasonable agreement. The temperature dependence down to 210 K has been reported in Refs. 1 and 2. They are in fair agreement at the shorter wavelengths, both studies reporting a significant decrease in absorption as the temperature is lowered. At the longer wavelengths they are in disagreement at low temperatures. For values at low temperatures the reader is referred to the original references.[1,2] Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CH_3CF_2 + Cl. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] D. Gillotay and P. C. Simon, J. Atmos. Chem. **12**, 269 (1991).
[2] J. J. Orlando, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Geophys. Res. **96**, 5013 (1991).
[3] C. Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

CH_3CFCl_2(HCFC-141b) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CFCl_2 + h\nu \rightarrow CH_3CFCl + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for CH_3CFCl_2 photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	83.8	210	2.1
2	64.1	2	1.4
4	47.4	4	0.88
6	34.0	6	0.57
8	23.8	8	0.37
200	16.4	220	0.24
2	11.1	2	0.16
4	7.4	4	0.10
6	4.9	6	0.07
8	3.2	8	0.04

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Fahr *et al.*[1] In this study[1] measurements were made in the gas phase (190–260 nm) and the liquid phase (230–260 nm) at 298 K. Correction factors were used to convert these liquid-phase values into accurate gas-phase values at the long wavelengths. Results reported in this study[1] are in very good agreement with those reported by Gillotay and Simon.[2] The results of Talukdar *et al.*[3] are lower at shorter wavelengths and higher at longer wavelengths. Gillotay and Simon[2] and Talukdar *et al.*[3] report the temperature dependence down to 210 K. For values at low temperatures the reader is referred to the original references.[2,3] Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield $CH_3CFCl + Cl$.

References

[1] A. Fahr, W. Braun, and M. J. Kurylo, J. Geophys. Res. **98**, 20467 (1993).
[2] D. Gillotay and P. C. Simon, J. Atmos. Chem. **12**, 269 (1991).
[3] R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **95**, 5815 (1991).

CH_3CCl_3 + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CCl_3 + h\nu \rightarrow CH_3CCl_2 + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for CH_3CCl_3 photolysis at 295 K and 210 K

	10^{20} σ/cm^2			10^{20} σ/cm^2	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
182	315	315	210	24.0	19.8
4	280	280	2	16.8	13.2
6	250	250	4	12.0	8.8
8	220	220	6	8.6	6.1
190	192	192	8	6.0	4.2
2	163	163	220	4.1	2.9
4	140	140	2	2.9	1.2
6	118	118	4	2.0	1.2
8	99	99	6	1.5	0.76
200	81	81	8	1.0	0.51
2	66	64	230	0.70	0.33
4	52	49	2	0.49	0.18
6	40	36	4	0.33	0.11
8	31	26	6	0.23	0.064
			8	0.15	0.036
			240	0.10	0.024

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K and at 210 K are the values reported by Vanlaethem-Meuree *et al.*[1] These values[1] are preferred over the substantially higher values reported by Hubrich and Stuhl,[2] in which study a correction was required for the presence of the UV-absorbing stabilizer 1,4-dioxane. In Ref. 1, absorption cross-section values are given for 295 K, 270 K, 250 K, 230 K, and 210 K. In a recent study Nayak *et al.*[3] reported measurements in the gas phase (160–240 nm) and the liquid phase (235–260 nm) over the temperature range 220–330 K. A wavelength shift procedure was used to convert the liquid-phase values into effective gas-phase values at the long wavelengths. The reported room temperature values[3] are in good agreement with those of Vanlaethem-Meuree *et al.*[1] in the range 210–240 nm, whereas in the 180–210 nm range they are 15% to 30% higher. Low temperature results are in relatively good agreement up to 230 nm. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CH_3CCl_2 + Cl.

References

[1] N. Vanlaethem-Meuree, J. Wisemberg, and P. C. Simon, Geophys. Res. Lett. **6**, 451 (1979).
[2] C. Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).
[3] A. K. Nayak, M. J. Kurylo, and A. Fahr, J. Geophys. Res. **100**, 11185 (1995).

CF_3CHFCl(HCFC-124) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CF_3CHFCl + h\nu \rightarrow CF_3CHF + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for CF_3CHFCl photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	0.77	210	0.018
2	0.55	2	0.012
4	0.39	4	0.008
6	0.27	6	0.006
8	0.18	8	0.004
200	0.13	220	0.003
2	0.086	2	0.002
4	0.060	4	0.002
6	0.040	6	0.001
8	0.027	8	0.001

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the averages of the values reported by Orlando *et al.*[1] and Gillotay and Simon,[2] which are in good agreement. Both studies investigated the temperature dependence down to about 210 K. The temperature dependences of Orlando *et al.*[1] are greater for shorter wavelengths (<200 nm) and less for the longer wavelengths than those reported by Gillotay and Simon.[2] The studies are in agreement on a significant decrease in absorption at the lowest temperature and the longer wavelengths, but over the same wavelength range and at the intermediate temperatures they are in poor agreement. For values at low temperatures the reader is referred to the original references.[1,2] Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF_3CHF + Cl.

References

[1] J. J. Orlando, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Geophys. Res. **96**, 5013 (1991).
[2] D. Gillotay and P. C. Simon, J. Atmos. Chem. **13**, 289 (1991).

CF_3CHCl_2(HCFC-123) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_3CHCl_2 + h\nu \rightarrow CF_3CHCl + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for CF_3CHCl_2 photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	59.0	210	1.8
2	44.5	2	1.3
4	32.9	4	0.87
6	23.6	6	0.61
8	16.9	8	0.40
200	11.9	220	0.28
2	8.3	2	0.20
4	5.7	4	0.14
6	4.0	6	0.10
8	2.7	8	0.07

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K, which are unchanged from our previous evaluation,[1] are the mean of the values reported by Gillotay and Simon[2] and Orlando *et al.*[3] The agreement between these studies over the wavelength range of preferred values is very good. Results of the recent study by Nayak *et al.*[4] are in good agreement with this recommendation, as are the results of Green and Wayne.[5] The temperature dependence down to about 210 K has been reported by Gillotay and Simon,[2] Orlando *et al.*,[3] and Nayak *et al.*[4] For values at low temperatures the reader is referred to the original references. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF_3CHCl + Cl.

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).

[2] D. Gillotay and P. C. Simon, J. Atmos. Chem. **12**, 269 (1991).

[3] J. J. Orlando, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Geophys. Res. **96**, 5013 (1991).

[4] A. K. Nayak, T. J. Buckley, M. J. Kurylo, and A. Fahr, J. Geophys. Res. **101**, 9055 (1996).

[5] R. G. Green and R. P. Wayne, J. Photochem. **6**, 375 (1976/77).

$CF_2ClCFCl_2$(CFC-113) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_2ClCFCl_2 + h\nu \rightarrow CF_2ClCFCl + Cl$ (1)	346 (est)	346
$\rightarrow CFCl_2CF_2 + Cl$ (2)	346 (est)	346

Preferred Values

Absorption cross-sections for $CF_2ClCFCl_2$ photolysis at 295 K and 210 K

	10^{20} σ/cm^2			10^{20} σ/cm^2	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
184	118	118	210	1.80	1.12
6	104	104	2	1.15	0.696
8	83.5	83.5	4	0.760	0.452
190	64.5	64.5	6	0.505	0.298
2	48.8	48.8	8	0.318	0.184
4	36.0	36.0	220	0.220	0.125
6	26.0	24.3	2	0.145	0.081
8	18.3	15.9	4	0.095	0.053
200	12.5	10.1	6	0.063	0.034
2	8.60	6.54	8	0.041	0.022
4	5.80	4.09	230	0.027	0.014
6	4.00	2.66			
8	2.65	1.68			

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Simon *et al.*[1] They are in very good agreement with the room temperature results of Chou *et al.*[2] and Hubrich and Stuhl,[3] who also made low temperature measurements. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield $CF_2ClCFCl$ + Cl or $CFCl_2CF_2$ + Cl. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, Ann. Geophysicae **6**, 239 (1988).

[2] C. C. Chou, R. J. Milstein, W. S. Smith, H. Vera Ruiz, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **82**, 1 (1978).

[3] C. Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

CF_2ClCF_2Cl(CFC-114) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_2ClCF_2Cl + h\nu \rightarrow CF_2ClCF_2 + Cl$	346 (est)	346

Preferred Values

Absorption cross-sections for CF_2ClCF_2Cl photolysis at 295 K and 210 K

	10^{20} σ/cm^2			10^{20} σ/cm^2	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
172	69	69	200	0.80	0.55
4	55	55	2	0.54	0.34
6	43	43	4	0.37	0.22
8	34	34	6	0.24	0.13
180	26	26	8	0.16	0.084
2	19.8	19.8	210	0.104	0.051
4	15.0	15.0	2	0.068	0.031
6	11.0	11.0	4	0.044	0.020
8	7.80	7.72	6	0.029	0.012
190	5.35	5.03	8	0.019	0.007
2	3.70	3.28	220	0.012	0.004
4	2.56	2.13			
6	1.75	1.39			
8	1.20	0.88			

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Simon *et al.*[1] They are in very good agreement with the room temperature results of Chou *et al.*[2] Hubrich and Stuhl[3] reported higher values and a smaller temperature dependence. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF_2ClCF_2 + Cl. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, Ann. Geophysicae **6**, 239 (1988).

[2] C. C. Chou, R. J. Milstein, W. S. Smith, H. Vera Ruiz, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **82**, 1 (1978).

[3] C. Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

CF_3CF_2Cl(CFC-115) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_3CF_2Cl + h\nu \rightarrow CF_3CF_2 + Cl$	346	346

Preferred Values

Absorption cross-sections for CF_3CF_2Cl photolysis at 295 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
172	5.65	190	0.27
4	4.05	2	0.19
6	2.85	4	0.13
8	2.05	6	0.090
180	1.45	8	0.063
2	1.05	200	0.044
4	0.75	2	0.031
6	0.53	4	0.021
8	0.38		

Comments on Preferred Values

The preferred values of the absorption cross-sections are the values reported by Simon *et al.*[1] In this study measurements were made down to 225 K, and the absorption cross-section values were found to be independent of temperature. They are in good agreement with the results of Hubrich and Stuhl,[2] who also made low temperature measurements. Earlier measurements of Chou *et al.*[3] are 50% higher. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF_3CF_2 + Cl. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, Ann. Geophysicae **6**, 239 (1988).

[2] C. Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).

[3] C. C. Chou, R. J. Milstein, W. S. Smith, H. Vera Ruiz, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **82**, 1 (1978).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CF_3CF_2CHCl_2$(HCFC-225ca) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_3CF_2CHCl_2 + h\nu \rightarrow CF_3CF_2CHCl + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for $CF_3CF_2CHCl_2$ photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
160	269	200	16
165	197	205	6.9
170	183	210	2.9
175	191	215	1.2
180	177	220	0.46
185	129	225	0.17
190	74	230	0.065
195	37	239	0.011

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Braun *et al.*[1] In the same study, absorption cross-section measurements in the liquid phase were made over the wavelength range 205–270 nm.[1] Correction factors were used to convert these liquid-phase values into gas-phase values. The combined set of gas-phase values for the wavelength range 170–270 nm were fitted[1] with the expression:

$$\log_{10}\sigma = -17.966 + 4.542\times10^{-2}X - 2.036\times10^{-3}X^2 + 1.042\times10^{-5}X^3 \text{ where } X = (\lambda - 160 \text{ nm})$$

Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF_3CF_2CHCl + Cl. The preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] W. Braun, A. Fahr, R. Klein, M. J. Kurylo, and R. E. Huie, J. Geophys. Res. **96**, 13009 (1991).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

CF_2ClCF_2CHFCl(HCFC-225cb) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_2ClCF_2CHFCl + h\nu \rightarrow CF_2ClCF_2CHF + Cl$ (1)	335 (est)	360
$\rightarrow CHFClCF_2CF_2 + Cl$ (2)	335 (est)	360

Preferred Values

Absorption cross-sections for CF_2ClCF_2CHFCl photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
160	188	185	9.1
165	145	190	3.5
170	91	195	1.4
175	47	200	0.63
180	21	205	0.33
		210	0.25

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Braun *et al.*[1] In the same study, absorption cross-section measurements in the liquid phase were made over the wavelength range 205–250 nm.[1] Correction factors were used to convert these liquid-phase values into gas-phase values. The combined set of gas-phase values for the wavelength range 170–250 nm were fitted with the expression:

$$\log_{10}\sigma = -17.714 - 2.175\times10^{-2}X - 1.484\times10^{-3}X^2 + 1.147\times10^{-5}X^3 \text{ where } X = (\lambda - 160 \text{ nm})$$

Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF_2ClCF_2CHF + Cl or $CHFClCF_2CF_2$ + Cl. The preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] W. Braun, A. Fahr, R. Klein, M. J. Kurylo, and R. E. Huie, J. Geophys. Res. **96**, 13009 (1991).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

HCOCl + $h\nu$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$HCOCl + h\nu \rightarrow HCO + Cl$	340 (est)	350

Preferred Values

Absorption cross-sections of HCOCl at the band maxima (298 K, 1013 mbar of N_2, spectral resolution 0.7 nm)

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
236.1	3.8	280.2	2.4
241.5	4.9	282.7	2.3
247.3	5.6	285.3	1.64
251.4	5.4	286.8	1.04
253.7	6.0	288.0	0.86
256.1	5.6	289.4	0.97
258.2	5.8	292.2	0.81
260.2	6.0	294.9	0.46
263.5	5.1	296.7	0.32
265.7	5.3	298.1	0.22
267.9	5.2	299.5	0.25
269.1	3.9	302.3	0.172
270.2	3.5	305.2	0.080
271.4	4.0	308.1	0.027
273.8	4.1	309.3	0.021
276.3	3.4	311.1	0.020
277.7	2.4	314.1	0.013
278.9	2.1	316.7	0.008
		318.7	0.007

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1992.[1] The preferred values of the absorption cross-sections at 298 K are those reported by Libuda *et al.*[2] These are the values of the absorption cross-sections at the absorption maxima and were measured at a spectral resolution of 0.7 nm. The absorption bands for $\lambda > 265$ nm became distinctly sharper when the spectral resolution was improved to 0.4 nm. The spectrum of HCOCl is similar to that of HCHO but is shifted to shorter wavelengths by 45 nm. Although there have been no quantum yield studies of HCOCl photolysis, it is reasonable to assume by analogy with the photolysis of $COCl_2$ that the primary photolysis pathway proceeds by breaking of the C-Cl bond to yield HCO + Cl.

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).
[2] H. G. Libuda, F. Zabel, E. H. Fink, and K. H. Becker, J. Phys. Chem. 94, 5860 (1990).

COFCl + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$COFCl + h\nu \rightarrow COF + Cl$	(1)	377	317
$\rightarrow COCl + F$	(2)	489	244
$\rightarrow CO + F + Cl$	(3)	517	231
$\rightarrow CFCl + O(^3P)$	(4)	656	182

Preferred Values

Absorption cross-sections for COFCl photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
186.0	15.6	207.3	10.8
187.8	14.0	209.4	9.9
189.6	13.4	211.6	9.0
191.4	12.9	213.9	7.9
193.2	12.7	216.2	6.9
195.1	12.5	218.6	5.8
197.0	12.4	221.0	4.8
199.0	12.3	223.5	3.8
201.0	12.5	226.0	2.9
203.0	12.0	228.6	2.2
205.1	11.5	231.2	1.6

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Chou *et al.*[1] over the wavelength range 186 to 199 nm and those reported in the recent study of Nolle *et al.*[2] at longer wavelengths. The spectrum shows little structure; the values listed are averages over 500 cm^{-1} intervals. Nolle *et al.*[2] reported values over the wavelength range 200–260 nm and the temperature range 298–223 K. Their room temperature values are in good agreement with those of Chou *et al.*[1] The effect of temperature on calculated photodissociation rates is negligible because no strong temperature dependence is observed in the atmospheric window region where photolysis occurs (190–230 nm). Hermann *et al.*[3] photolyzed COFCl at 193 nm and analyzed the parent and products by FTIR spectroscopy. They could explain their results[3] using only channels (1) and (3), and reported a total quantum yield of 1.0 independent of pressure from 10 to 900 mbar N_2. The relative contribution of channels (1) and (3) was found to depend on pressure with an equal contribution of the two channels at 900 mbar N_2.

References

[1] G. C. Chou, G. Crescentini, H. Vera-Ruiz, W. S. Smith, and F. S. Rowland, Results presented at the 173rd American Chemical Society National Meeting, New Orleans, March, 1977.

[2] A. Nolle, H. Heydtmann, R. Meller, W. Schneider, and G. K. Moortgat, Geophys. Res. Lett. **20**, 707 (1993).

[3] M. Hermann, A. Nolle, and H. Heydtmann, Chem. Phys. Lett. **226**, 559 (1994).

$COCl_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		ΔH°/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$COCl_2 + h\nu \rightarrow COCl + Cl$	(1)	324	369
$\rightarrow CO + 2\,Cl$	(2)	352	340
$\rightarrow CCl_2 + O(^3P)$	(3)	707	169

Preferred Values

Absorption cross-sections for $COCl_2$ photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
184.4	234	211.6	13.3
186.0	186	213.9	12.6
187.8	146	216.2	12.3
189.6	116	218.6	12.2
191.4	90.3	221.0	12.2
193.2	71.5	223.5	12.4
195.1	52.4	226.0	12.7
197.0	39.9	228.6	13.1
199.0	31.2	231.2	13.4
201.0	25.2	233.9	13.6
203.0	20.9	236.7	13.1
205.1	17.9	239.5	12.5
207.3	15.8	242.4	11.6
209.4	14.3		

Quantum Yield for $COCl_2$ Photolysis at 298 K

$\phi = 1.0$ for $\lambda > 184$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported in the recent study of Gillotay *et al.*[1] The spectrum is a continuum; the values listed are averaged over 500 cm^{-1} intervals. These results[1] are in good agreement with the earlier results of Chou *et al.*[2] Gillotay *et al.*[1] reported values over the wavelength range 170 to 310 nm and the temperature range 295–210 K. The temperature effect is only significant at longer wavelengths ($\lambda > 250$ nm). The observations of Wijnen,[3] Heicklen,[4] and earlier investigators[5] show that process (1) is the primary photolysis pathway.

References

[1] D. Gillotay, P. C. Simon, and L. Dierickx, Aeronomica Acta, **A368** (1993), Institut d'Aeronomie Spatiale de Belgique, Brussels, Belgium; presented at Quadrennial Ozone Symposium, Charlottesville, Virginia, June, 1992.

[2] G. C. Chou, G. Crescentini, H. Vera-Ruiz, W. S. Smith, and F. S. Rowland, Results presented at the 173rd American Chemical Society National Meeting, New Orleans, March, 1977.

[3] W. H. Wijnen, J. Am. Chem. Soc. **83**, 3014 (1961).

[4] J. Heicklen, J. Am. Chem. Soc. **87**, 445 (1965).

[5] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966), p. 231.

$CF_2ClCHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°/kJ\cdot mol^{-1}$	$\lambda_{threshold}/nm$
$CF_2ClCHO + h\nu \rightarrow CF_2Cl + HCO$ (1)		
$\rightarrow CF_2ClCO + H$ (2)		
$\rightarrow CHF_2Cl + CO$ (3)		

Absorption cross-section data

Wavelength range/nm	References	Comments
240–370	Rattigan and Cox, 1993[1]	(a)

Quantum yield data

There are no reported quantum yield data.

Comments

(a) Absolute absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 245–298 K. The UV spectrum of difluorochloroacetaldehyde shows a broad band, centered at 300 nm and extending out to 365 nm. Values of σ were given at 5 nm intervals at 245 K and 298 K.

Preferred Values

Absorption cross-sections at 298 and 245 K

	$10^{20}\ \sigma/\text{cm}^2$	
Wavelength/nm	298 K	245 K
240	0.384	0.417
245	0.703	0.751
250	1.184	1.276
255	1.910	2.021
260	2.875	3.082
265	4.181	4.451
270	5.802	6.154
275	7.623	8.108
280	9.651	10.29
285	11.61	12.32
290	13.48	14.37
295	14.74	15.59
300	15.67	16.70
305	15.49	16.08
310	15.18	15.99
315	13.22	13.80
320	11.63	12.13
325	9.367	10.03
330	6.553	6.583
335	4.800	4.840
340	2.784	2.944
345	1.516	1.393
350	0.730	0.599
355	0.113	0.070
360	0.034	0.024
365	0.011	0.007
370	0.000	0.000

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data reported by Rattigan and Cox.[1] There are no data on the quantum yields but, by analogy with acetaldehyde which shows a similar absorption spectrum, photodissociation is expected to be predominantly by channel (1).

References

[1] O. Rattigan and R. A. Cox, Final Report to SPA-AFEAS, Washington, DC (1993).

$CFCl_2CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$CFCl_2CHO + h\nu \rightarrow CFCl_2 + HCO$	(1)		
$\rightarrow CFCl_2CO + H$	(2)		
$\rightarrow CHFCl_2 + CO$	(3)		

Absorption cross-section data

Wavelength range/nm	References	Comments
200–340	Rattigan and Cox, 1993[1]	(a)

Quantum yield data

There are no reported quantum yield data.

Comments

(a) Absolute absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 253–296 K. The UV spectrum of dichlorofluoroacetaldehyde shows a broad band, centered at 295 nm and extending out to 365 nm. Values of σ were given at 5 nm intervals at 296 K and 253 K.

Preferred Values

Absorption cross-sections at 296 and 253 K

	$10^{20}\ \sigma/\text{cm}^2$	
Wavelength/nm	296 K	253 K
240	0.795	0.546
245	1.069	0.934
250	1.587	1.541
255	2.377	2.405
260	3.470	3.569
265	4.853	5.022
270	6.514	6.753
275	8.343	8.662
280	10.10	10.48
285	11.79	12.22
290	12.98	13.38
295	13.76	14.16
300	13.60	13.87
305	12.91	12.91
310	11.52	11.52
315	9.783	9.427
320	7.969	7.733
325	5.599	5.159
330	3.904	3.654
335	2.449	2.108
340	1.229	1.048
345	0.623	0.446
350	0.244	0.164
355	0.041	0.025
360	0.016	0.012
365	0.007	0.004
370	0.000	0.000

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data reported by Rattigan and Cox.[1] There are no data on the quantum yields but, by analogy with acetaldehyde which shows a similar absorption spectrum, photodissociation is expected to be predominantly by channel (1).

References

[1] O. Rattigan and R. A. Cox, Final Report to SPA-AFEAS, Washington, DC (1993).

$CCl_3CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$CCl_3CHO + h\nu \rightarrow CCl_3 + HCO$ (1)		
$\rightarrow CCl_3CO + H$ (2)		
$\rightarrow CHCl_3 + CO$ (3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–340	Rattigan *et al.*, 1993[1]	(a)

Quantum yield data

There are no reported quantum yield data.

Comments

(a) Absolute absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 240–300 K. The UV spectrum of trichloroacetaldehyde shows a broad band, centered at 290 nm and extending out to 360 nm. Values of σ were given at 5 nm intervals at 296 K and 243 K. A second absorption band appears at <230 nm.

Preferred Values

Absorption cross-sections at 296 and 243 K

	$10^{20}\ \sigma/\text{cm}^2$	
Wavelength/nm	296 K	243 K
200	115.1	110.7
205	86.14	81.89
210	48.19	43.20
215	23.88	20.32
220	10.92	9.179
225	4.759	3.527
230	2.034	1.264
235	0.944	0.430
240	0.774	0.418
245	1.135	0.882
250	1.827	1.633
255	2.799	2.659
260	3.977	3.910
265	5.360	5.388
270	6.722	6.878
275	8.012	8.368
280	9.318	9.625
285	10.08	10.35
290	10.32	10.62
295	9.886	10.06
300	9.019	9.245
305	7.671	7.602
310	6.074	5.942
315	4.572	4.446
320	3.063	2.790
325	1.901	1.741
330	1.121	0.951
335	0.498	0.322
340	0.194	0.114
345	0.086	0.043
350	0.020	0.004
355	0.002	0.000
360	0.000	0.000

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data reported by Rattigan *et al.*[1] There are no data on the quantum yields but, by analogy with acetaldehyde which shows a similar absorption spectrum, photodissociation is expected to be predominantly by channel (1).

References

[1] O. V. Rattigan, O. Wild, R. L. Jones, and R. A. Cox, J. Photochem. Photobiol. A: Chem. 73, 1 (1993).

$CF_3COCl + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°/kJ\cdot mol^{-1}$	$\lambda_{threshold}/nm$
$CF_3COCl + h\nu \rightarrow CF_3 + COCl$ (1) $\rightarrow CF_3CO + Cl$ (2)		

Absorption cross-section data

Wavelength range/nm	References	Comments
200–330	Meller, Boglu, and Moortgat, 1993[1]	(a)

Quantum yield data

Measurement	Wavelength/ nm	Reference	Comments
$\phi(1)+\phi(2)=0.955\pm0.06$	254	Meller, Boglu, and Moortgat, 1993[1]	(b)

Comments

(a) Absolute absorption cross-sections were measured using a diode array spectrometer over the temperature range 223–298 K. The UV spectrum of trifluoroacetyl chloride shows two overlapping bands, the first having a maximum at 255 nm ($\sigma=6.78\times10^{-19}$ cm^2 molecule^{-1}), and the second at $\lambda<200$ nm. There is significant absorption at wavelengths $\lambda>300$ nm, where the cross-sections become increasingly temperature dependent. Values of σ were given at 5 nm intervals at 298 K and 240 K as well as temperature coefficients in the long wavelength tail at $\lambda>270$ nm.

(b) Average of 10 measurements of the overall loss of CF_3COCl during photolysis in air ($\phi=0.95\pm0.05$) and 7 measurements in N_2 ($\phi=0.96\pm0.06$) at 298 K, relative to the loss of $COCl_2$ for which $\phi=1$. No pressure dependence was observed in the total pressure range 50–400 Torr.

Preferred Values

Absorption cross-sections at 298 K and 223 K

	$10^{20}\ \sigma/cm^2$		
λ/nm	298 K	223 K	$10^3\times B/K^{-1}$
205	13.51	11.02	2.72
210	3.58	2.71	3.72
215	1.72	1.50	1.76
220	1.85	1.81	0.28
225	2.51	2.50	0.07
230	3.38	3.35	0.10
235	4.32	4.27	0.15
240	5.23	5.16	0.18
245	6.03	5.96	0.15
250	6.56	6.45	0.23
255	6.71	6.55	0.32
260	6.49	6.27	0.45
265	5.90	5.62	0.65
270	5.03	4.72	0.82
275	4.02	3.70	1.11
280	3.00	2.69	1.45
285	2.07	1.77	2.11
290	1.33	1.09	2.60
295	0.778	0.598	3.51
300	0.406	0.300	4.03
305	0.190	0.127	5.33
310	0.074	0.040	8.37
315	0.025	0.009	13.36
320	0.008	0.002	19.69
325	0.003		

[a] Temperature dependence: $\log_e\{\sigma(T)/\sigma(293)\}=B(T-293)$.

Quantum Yields

$\phi(1)+\phi(2)=1.0$ over the wavelength range 200–315 nm.

Comments on Preferred Values

The data of Meller *et al.*[1] are in generally excellent agreement with the earlier results of Rattigan *et al.*[2] and Jemi-Alade *et al.*,[3] except in the region of minimum absorption near 220 nm. The preferred values for the cross-sections are those reported by Meller *et al.*[1] They differ significantly from the previously recommended values of Rattigan *et al.*[2] only in the range 215–235 nm. The temperature-dependence of the cross-section is also from Meller *et al.*[1] The quantum yield is based on the measurements of Meller *et al.*[1]

References

[1] R. Meller, D. Boglu, and G. K. Moortgat, "Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere," STEP-HALOCSIDE/AFEAS Workshop, Dublin, Eire, March 23–25, 1993, pp. 130–138.

[2] O. V. Rattigan, O. Wild, R. L. Jones, and R. A. Cox, J. Photochem. Photobiol. A: Chem. **73**, 1 (1993).

[3] A. A. Jemi-Alade, P. D. Lightfoot, and R. Lesclaux, Chem. Phys. Lett. **179**, 119 (1991).

4.8. Bromine Species

O + HOBr → HO + BrO

$\Delta H° = -35$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.5\pm0.4)\times10^{-11}$	298	Monks *et al.*, 1993[1]	(a)
Reviews and Evaluations			
2.5×10^{-11}	298	NASA, 1994[2]	(b)

Comments

(a) Discharge flow system with MS detection. The pseudo-first-order decays of the HOBr concentration in the presence of excess concentrations of O(^{3}P) atoms were monitored.

(b) Based on the results of Monks *et al.*[1]

Preferred Values

$k = 2.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.5$ at 298 K.

Comments on Preferred Values

The preferred value is based on the room temperature results of Monks *et al.*[1] This is the only experimental study of this reaction. Note that the rate coefficient for this reaction is a factor of 200 greater than the rate coefficient for the corresponding reaction of O(^{3}P) atoms with HOCl (this evaluation).

References

[1] P. S. Monks, F. L. Nesbitt, M. Scanlon, and L. J. Stief, J. Phys. Chem. **97**, 11699 (1993).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

O + BrO → O$_2$ + Br

$\Delta H° = -262$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.9\times10^{-11}\exp[(230\pm76)/T]$	233–328	Thorn *et al.* 1995[1]	(a)
4.1×10^{-11}	298		
Reviews and Evaluations			
3×10^{-11}	298	IUPAC, 1992[2]	(b)
$1.7\times10^{-11}\exp(260/T)$	230–330	NASA, 1994[3]	(c)

Comments

(a) Dual laser flash photolysis/long path absorption/resonance fluorescence technique.

(b) Based on the results of Clyne *et al.*[4]

(c) Based on the results of Thorn *et al.*[1] (then unpublished).

Preferred Values

$k = 4.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.9\times10^{-11}\exp(230/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–330 K.

Reliability

$\Delta\log k = \pm0.2$ at 298 K.

$\Delta(E/R) = \pm150$ K.

Comments on Preferred Values

The preferred values are based on the results reported by Thorn *et al.*[1] using a dual laser flash photolysis/long path absorption/resonance fluorescence technique in which the decay of O(^{3}P) in the presence of excess BrO was monitored. Clyne *et al.*[4] reported an approximately 40% lower room temperature value.

References

[1] R. P. Thorn, J. M. Crunkhite, J. M. Nicovich, and P. H. Wine, J. Chem. Phys. **102**, 4131 (1995).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] M. A. A. Clyne, P. B. Monkhouse, and L. W. Townsend, Int. J. Chem. Kinet. **8**, 425 (1976).

$Br + HO_2 \rightarrow HBr + O_2$

$\Delta H^\circ = -163\ kJ\cdot mol^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 2.0\times10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k = 1.4\times10^{-11}\ \exp(-590/T)\ molecule^{-1}\ s^{-1}$ over the temperature range 260–390 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This recommendation is based on results obtained over the 260–390 K temperature range by Toohey *et al.*,[1] using a discharge flow system with LMR detection to monitor the decays of HO_2 radicals in excess Br. The value determined by Laverdet *et al.*[2] is in good agreement with this recommendation. Laverdet *et al.*[2] have reinterpreted previous indirect measurements conducted in the same laboratory, by Poulet *et al.*,[3] to give a range of values higher than had been reported[3] and in agreement with the present recommendation. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] D. W. Toohey, Wm. H. Brune, and J. G. Anderson, J. Phys. Chem. **91**, 1215 (1987).

[2] G. Laverdet, G. Le Bras, A. Mellouki, and G. Poulet, Chem. Phys. Lett. **172**, 430 (1990).

[3] G. Poulet, G. Laverdet, and G. Le Bras, J. Chem. Phys. **80**, 1922 (1984).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Br + H_2O_2 \rightarrow HBr + HO_2$ (1)
$\rightarrow HOBr + HO$ (2)

$\Delta H^\circ(1) = 2.7\ kJ\cdot mol^{-1}$

$\Delta H^\circ(2) = 14\ kJ\cdot mol^{-1}$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = < 5\times10^{-16}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

Comments on Preferred Values

The upper limit to the preferred value is based on the data of Toohey *et al.*,[1] who also obtained the same upper limit at 378 K using a discharge flow–resonance fluorescence/LMR technique. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.[2]

References

[1] D. W. Toohey, Wm. H. Brune, and J. G. Anderson, J. Phys. Chem. **91**, 1215 (1987).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Br + O_3 \rightarrow BrO + O_2$

$\Delta H^\circ = -130\ kJ\cdot mol^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.7 \times 10^{-11} \exp(-800/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 195–392 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The recommended Arrhenius expression is based on a fit to the results of Toohey *et al.*,[1] Clyne and Watson,[2] Leu and DeMore,[3] Michael *et al.*,[4] Michael and Payne,[5] and Nicovich *et al.*[6] The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[7]

References

[1] D. W. Toohey, W. H. Brune, and J. G. Anderson, Int. J. Chem. Kinet. **20**, 131 (1988).

[2] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **71**, 336 (1975).

[3] M. T. Leu and W. B. DeMore, Chem. Phys. Lett. **48**, 317 (1977).

[4] J. V. Michael, J. H. Lee, W. A. Payne, and L. J. Stief, J. Chem. Phys. **68**, 4093 (1978).

[5] J. V. Michael and W. A. Payne, Int. J. Chem. Kinet. **11**, 799 (1979).

[6] J. M. Nicovich, K. D. Kreutter, and P. H. Wine, Int. J. Chem. Kinet. **22**, 399 (1990).

[7] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Br + NO_2 + M \rightarrow BrNO_2 + M$

$\Delta H° = -82$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 4.2 \times 10^{-31} (T/300)^{-2.4} [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The recommended values of Ref. 1 are consistent with theoretical predictions. The falloff curves are represented with $F_c = 0.55$ at 298 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 2.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.4$ over the range 200–300 K.

Comments on Preferred Values

See comments on k_0. There is only a single determination of k_∞, but the measured falloff curve appears well behaved with rate coefficients close to those of the reactions I + NO + M and I + NO_2 + M (see this evaluation). These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[2]

References

[1] K. D. Kreutter, J. M. Nicovich, and P. H. Wine, J. Phys. Chem. **95**, 4020 (1991).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Br + OClO \rightarrow BrO + ClO$

$\Delta H° = 19$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=3.4\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k=2.6\times10^{-11}$ $\exp(-1300/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200–450 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The preferred value at 298 K is the mean of the values reported by Toohey[1] and Clyne and Watson.[2] The latter study[2] required correction for the effect of the reverse reaction on the decay of OClO, which was not taken into account in the earlier study of Clyne and Coxon[3] and which is therefore disregarded. The temperature dependence of Toohey[1] is accepted. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] D. W. Toohey, "Kinetic and Mechanistic Studies of Reactions of Bromine and Chlorine Species Important in the Earth's Stratosphere," Ph.D. Thesis, Harvard University, Cambridge, MA (1988).
[2] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **73**, 1169 (1977).
[3] M. A. A. Clyne and J. A. Coxon, Proc. R. Soc. London, Ser. A **298**, 424 (1967).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Br + Cl_2O \rightarrow BrCl + ClO$

$\Delta H^\circ=-77.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.1\times10^{-11}\exp[-(435\pm30)/T]$	233–404	Stevens and Anderson, 1992[1]	(a)
$(4.8\pm0.2)\times10^{-12}$	298		
Reviews and Evaluations			
$2.1\times10^{-11}\exp(-520/T)$	220–298	IUPAC, 1992[2]	(b)
$2.1\times10^{-11}\exp(-470/T)$	220–400	NASA, 1994[3]	(c)

Comments

(a) Discharge flow system. The pseudo-first-order decays of Br atoms in excess Cl_2O were measured, with detection by resonance fluorescence.
(b) Based on the results of Sander and Friedl.[4]
(c) Based on the results of Stevens and Anderson[1] and Sander and Friedl.[4]

Preferred Values

$k=4.3\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k=2.1\times10^{-11}$ $\exp(-470/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 220–400 K.

Reliability

$\Delta\log k=\pm0.1$ at 298 K.
$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The preferred value is based on the results reported by Stevens and Anderson[1] and Sander and Friedl.[4] These results obtained using totally different techniques[1,4] are in good agreement. The significantly lower value (by a factor of 4) reported earlier by Basco and Dogra[5] has been rejected. In that same study, Basco and Dogra[5] reported a value of $k(Cl + Cl_2O)$ more than two orders of magnitude less than that recommended in this evaluation, suggesting the possibility of a systematic error in their method of determination of ClO radical concentrations.

References

[1] P. S. Stevens and J. G. Anderson, J. Phys. Chem. **96**, 1708 (1992).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] S. P. Sander and R. R. Friedl, J. Phys. Chem. **93**, 4764 (1989).
[5] N. Basco and S. K. Dogra, Proc. R. Soc. London, Ser. A **323**, 401 (1971).

$Br + Cl_2O_2 \rightarrow BrCl + ClOO$

$\Delta H^\circ=-127.4$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=3.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on results of the discharge flow-mass spectrometric study of Friedl.[1] The preferred value is identical to that in our previous evaluation, IUPAC. 1992.[2]

References

[1] R. R. Friedl, unpublished data (1991).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Br + HCHO \rightarrow HBr + HCO$

$\Delta H^\circ=2.2$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=1.1\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.7\times10^{-11}\exp(-800/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 223–480 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.

$\Delta(E/R)=\pm250$ K.

Comments on Preferred Values

The preferred rate expression is obtained from a least-squares analysis of the absolute rate coefficient data of Nava *et al.*[1] and Poulet *et al.*,[2] which are in reasonably good agreement. The Arrhenius expression is identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] D. F. Nava, J. V. Michael, and L. J. Stief, J. Phys. Chem. **85**, 1896 (1981).

[2] G. Poulet, G. Laverdet, and G. Le Bras, J. Phys. Chem. **85**, 1892 (1981).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$Br + CH_3CHO \rightarrow HBr + CH_3CO$

$\Delta H^\circ=-6.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=3.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.3\times10^{-11}\exp(-360/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–400 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute rate coefficients of Nicovich *et al.*[1] and Islam *et al.*[2] and the relative rate coefficient of Niki *et al.*[3] The temperature dependence is that measured by Nicovich *et al.*,[1] with the *A* factor being adjusted to yield the 298 K preferred value. The preferred room temperature rate coefficient is consistent with the recent relative rate studies of Barnes *et al.*[4] and Wallington *et al.*[5] [which do not provide definitive data concerning the rate constant for the reaction of Br atoms with CH_3CHO]. The preferred values are identical to our previous evaluation, IUPAC, 1992.[6]

References

[1] J. M. Nicovich, C. J. Shackelford, and P. H. Wine, J. Photochem. Photobiol., A: Chemistry, **51**, 141 (1990).

[2] T. S. A. Islam, R. M. Marshall, and S. W. Benson, Int. J. Chem. Kinet. **16**, 1161 (1984).

[3] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **17**, 525 (1985).

[4] I. Barnes, V. Bastian, K. H. Becker, R. Overath, and Z. Tong, Int. J. Chem. Kinet. **21**, 499 (1989).

[5] T. J. Wallington, L. M. Skewes, W. O. Siegl, and S. M. Japar, Int. J. Chem. Kinet. **21**, 1069 (1989).

[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + HBr \rightarrow H_2O + Br$

$\Delta H^\circ = -132.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.97\pm0.46)\times10^{-11}$	170	Sims *et al.*, 1995[1]	(a)
$(1.16\pm0.04)\times10^{-11}$	295		
Reviews and Evaluations			
1.1×10^{-11}	249–416	IUPAC, 1992[2]	(b)
1.1×10^{-11}	249–416	NASA, 1994[3]	(b)

Comments

(a) Pulsed laser photolysis system with LIF detection of HO radicals, using an isentropic expansion of gas through a Laval nozzle to provide a collimated flow of cold gas at a uniform temperature, density, and velocity. Experiments were carried out over the temperature range 23–295 K, with the measured rate coefficient decreasing with increasing temperature from $(1.07 \pm0.4)\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 23 K to $(1.16 \pm0.04)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 295 K. Combined with the rate coefficients of Ravishankara *et al.*,[4] the temperature-dependent expression $k=(1.26\pm0.24) \times10^{-11}$ $(T/298)^{-(0.86\pm0.10)}$ cm^3 molecule^{-1} s^{-1} was derived.

(b) Based on the absolute rate coefficients of Ravishankara *et al.*,[4,5] Jourdain *et al.*,[6] and Cannon *et al.*[7]

Preferred Values

$k=1.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=1.1\times10^{-11}$ $(T/298)^{-0.8}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta\log k = \pm0.10$ at 298 K.
$\Delta n = ^{+0.8}_{-0.2}$

Comments on Preferred Values

The recent absolute rate study of Sims *et al.*[1] yields rate coefficients which exhibit a significant negative temperature dependence over the temperature range 23–295 K. In contrast, the absolute rate coefficients measured by Ravishankara *et al.*[4] over the temperature range 249–416 K were independent of temperature within the experimental uncertainties.

The preferred 298 K rate coefficient is an average of the room temperature rate coefficients of Ravishankara *et al.*,[4,5] Jourdain *et al.*,[6] Cannon *et al.*,[7] and Sims *et al.*[1] The temperature dependence is obtained from the rate coefficients of Sims *et al.*[1] over the temperature range 23–295 K. The preferred rate expression predicts rate coefficients at 249 K and 416 K of 1.27×10^{-11} cm^3 molecule^{-1} s^{-1} and 8.4×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively, with that at 249 K being in excellent agreement with the rate coefficient measured by Ravishankara *et al.*[4] [$(1.31\pm0.08)\times10^{-11}$ cm^3 molecule^{-1} s^{-1}] and that at 416 K being 30% lower than that measured by Ravishankara *et al.*[4] The uncertainties on the values of n in $k=A\ (T/298)^{-n}$ encompass a temperature-independent rate coefficient.

References

[1] I. R. Sims, I. W. M. Smith, D. C. Clary, P. Bocherel, and B. R. Rowe, J. Chem. Phys. **102**, 1748 (1995).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

[4] A. R. Ravishankara, P. H. Wine, and J. R. Wells, J. Chem. Phys. **83**, 447 (1985).

[5] A. R. Ravishankara, P. H. Wine, and A. O. Langford, Chem. Phys. Lett. **63**, 479 (1979).

[6] J. L. Jourdain, G. Le Bras, and J. Combourieu, Chem. Phys. Lett. **78**, 483 (1981).

[7] B. D. Cannon, J. S. Robertshaw, I. W. M. Smith, and M. D. Williams, Chem. Phys. Lett. **105**, 380 (1984).

$HO + Br_2 \rightarrow HOBr + Br$

$\Delta H^\circ = -8$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=4.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=1.2\times10^{-11}$ exp(400/T) cm^3 molecule^{-1} s^{-1} over the temperature range 260–360 K.

Reliability
$\Delta\log k=\pm0.15$ at 298 K.
$\Delta(E/R)=\pm400$ K.

Comments on Preferred Values

The rate constant is reasonably well determined at room temperature, and the recommended value is the mean of those reported in Refs. 1–4. Boodaghians *et al.*[2] found a near zero temperature dependence over the range 262–303 K. In contrast, the data of Toohey[3] display a significant negative temperature dependence in the range 260–360 K. The latter result is preferred, and the recommendation for E/R is based on this study.[3] Loewenstein and Anderson[1] determined that the products are exclusively Br + HOBr. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[5]

References

[1] L. M. Loewenstein and J. G. Anderson, J. Phys. Chem. **88**, 6277 (1984).
[2] R. B. Boodaghians, I. W. Hall, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **83**, 529 (1987).
[3] D. W. Toohey, private communication (1988).
[4] G. Poulet, G. Laverdet, and G. Le Bras, Chem. Phys. Lett. **94**, 129 (1983).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + $CH_3Br \rightarrow H_2O + CH_2Br$

$\Delta H°=-74.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.86×10^{-12} exp[$-(1230\pm150)/T$]	248–390	Chichinin *et al.*, 1994[1]	(a)
$(3.03\pm0.45)\times10^{-14}$	298		
Relative Rate Coefficients			
3.84×10^{-18} T^2 exp[$-(692\pm46)/T$]	298–360	Hsu and DeMore, 1994[2]	(b)
3.16×10^{-14}	298		
Reviews and Evaluations			
1.9×10^{-12} exp($-1240/T$)	240–300	IUPAC, 1992[3]	(c)
3.62×10^{-18} T^2 exp($-711/T$)	233–400	Atkinson, 1994[4]	(d)
4.0×10^{-12} exp($-1470/T$)	233–400	NASA, 1994[5]	(e)

Comments

(a) Discharge flow system with EPR detection of HO radicals.

(b) Relative rate method. HO radicals were generated from the UV photolysis of O_3 in the presence of water vapor, in O_3-H_2O-CH_3Br-CH_3CHF_2-O_2-N_2 mixtures. The concentrations of CH_3Br and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + CH_3Br)/k(HO + CH_3CHF_2) $=(1.94\pm0.28)$ exp[$-(232\pm46)/T$] is placed on an absolute basis by use of a rate coefficient of k(HO + CH_3CHF_2) $=1.98\times10^{-18}$ T^2 exp($-460/T$) cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Derived from the absolute rate coefficients of Mellouki *et al.*[6] and Zhang *et al.*[7]

(d) Derived from the absolute rate coefficients of Mellouki *et al.*[6] and Zhang *et al.*,[7] using the three parameter equation $k=CT^2$ exp($-D/T$).

(e) Based on the rate coefficients of Mellouki *et al.*,[6] Zhang *et al.*,[7] Chichinin *et al.*,[1] and Hsu and DeMore.[2]

Preferred Values

$k=2.9\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=1.7\times10^{-12}$ exp($-1215/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability
$\Delta\log k=\pm0.08$ at 298 K.
$\Delta(E/R)=\pm150$ K.

Comments on Preferred Values

The recent absolute rate coefficient measurements of Mellouki *et al.*,[6] Zhang *et al.*,[7] and Chichinin *et al.*,[1] which are in excellent agreement, are significantly lower than those previously determined by Howard and Evenson[8] and Davis *et al.*[9] The relative rate coefficients of Hsu and DeMore[2] are also in excellent agreement with the absolute rate coefficients of Mellouki *et al.*,[6] Zhang *et al.*,[7] and Chichinin *et al.*[1] A unit-weighted least-squares analysis of the rate coefficients of Mellouki *et al.*,[6] Zhang *et al.*,[7] and Chichinin *et al.*,[1] using the three parameter expression $k=CT^2$ exp($-D/T$), leads to $k=3.44\times10^{-18}$ T^2 exp($-687/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 233–400 K. The preferred Arrhenius expression, $k=A\ \exp(-B/T)$, is centered at 265 K and is derived from three parameter expression with $A=C\ e^2\ T^2$ and $B=D+2T$.

References

[1] A. Chichinin, S. Téton, G. Le Bras, and G. Poulet, J. Atmos. Chem. **18**, 239 (1994).

[2] K.-J. Hsu and W. B. DeMore, Geophys. Res. Lett. **21**, 805 (1994).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

[6] A. Mellouki, R. K. Talukdar, A.-M. Schmoltner, T. Gierczak, M. J. Mills, S. Solomon, and A. R. Ravishankara, Geophys. Res. Lett. **19**, 2059 (1992).

[7] Z. Zhang, R. D. Saini, M. J. Kurylo, and R. E. Huie, Geophys. Res. Lett. **19**, 2413 (1992).

[8] C. J. Howard, and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).

[9] D. D. Davis, G. Machado, B. C. Conaway, Y. Oh, and R. T. Watson, J. Chem. Phys. **65**, 1268 (1976).

$HO + CH_2Br_2 \rightarrow H_2O + CHBr_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.91\times10^{-12}\exp[-(840\pm100)/T]$	243–380	Mellouki *et al.*, 1992[1]	(a)
$(1.13\pm0.11)\times10^{-13}$	298		
Reviews and Evaluations			
$1.9\times10^{-12}\exp(-840/T)$	243–380	NASA, 1994[2]	(b)

Comments

(a) Laser photolysis system with LIF detection of HO radicals.

(b) Based on the absolute rate coefficients of Mellouki *et al.*[1]

Preferred Values

$k=1.1\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=1.5\times10^{-12}\exp(-775/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k=\pm0.20$ at 298 K.
$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The absolute rate coefficients of Mellouki *et al.*[1] have been fitted to the three parameter equation $k=CT^2\times\exp(-D/T)$, resulting in $k=2.86\times10^{-18}\ T^2\exp(-246/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 243–380 K. The preferred Arrhenius expression, $k=A\ \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A=C\ e^2\ T^2$ and $B=D+2T$.

References

[1] A. Mellouki, R. K. Talukdar, A.-M. Schmoltner, T. Gierczak, M. J. Mills, S. Solomon, and A. R. Ravishankara, Geophys. Res. Lett. **19**, 2059 (1992).

[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$HO + CHF_2Br$(Halon 1201) → $H_2O + CF_2Br$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
9.3×10^{-13} exp[$-(1326\pm33)/T$]	298–460	Orkin and Khamaganov, 1993[1]	(a)
$(1.10\pm0.09)\times10^{-14}$	298		
Relative Rate Coefficients			
3.18×10^{-20} $T^{2.58}$ exp[$-(622\pm31)/T$]	283-368	Hsu and DeMore, 1995[2]	(b)
9.60×10^{-15}	298		
Reviews and Evaluations			
7.7×10^{-13} exp($-1310/T$)	240-300	IUPAC, 1992[3]	(c)
1.48×10^{-18} T^2 exp($-779/T$)	233-432	Atkinson, 1994[4]	(d)
1.1×10^{-12} exp($-1400/T$)	233-460	NASA, 1994[5]	(e)

Comments

(a) Discharge flow system with EPR detection of HO radicals.

(b) Relative rate method. HO radicals were generated by the UV photolysis of O_3 in the presence of water vapor in O_3-H_2O-CHF_2Br-CH_4-O_2-N_2 mixtures. The concentrations of CHF_2Br and CH_4 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CHF_2Br)/k(HO + CH_4) = (0.33\pm0.03)\times\exp[(460\pm31)/T]$ is placed on an absolute basis by using a rate coefficient of $k(HO + CH_4) = 9.65\times10^{-20}\ T^{2.58}\ \exp(-1082/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Based on the absolute rate coefficients of Talukdar *et al.*[6]

(d) Based on the absolute rate coefficients of Talukdar *et al.*,[6] using the three parameter equation $k = CT^2 \times\exp(-D/T)$.

(e) Derived from the absolute rate coefficients of Talukdar *et al.*[6] and Orkin and Khamaganov[1] and the relative rate coefficients of Hsu and DeMore.[2]

Preferred Values

$k = 9.8\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.1\times10^{-13}\ \exp(-1315/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240 300 K.

Reliability

$\Delta\log k = \pm0.10$ at 298 K.

$\Delta(E/R) = \pm150$ K.

Comments on Preferred Values

The absolute and relative rate coefficients of Talukdar *et al.*,[6] Orkin and Khamaganov,[1] and Hsu and DeMore[2] are in excellent agreement, but are significantly lower than the absolute rate coefficients of Brown *et al.*[7] The absolute rate coefficients of Talukdar *et al.*[6] and Orkin and Khamaganov[1] have been fitted to the three parameter equation $k = CT^2 \times\exp(-D/T)$, resulting in $k = 1.56\times10^{-18}\ T^2\ \exp(-786/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 233–460 K. The preferred Arrhenius expression, $k = A\ \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C\ e^2\ T^2$ and $B = D + 2T$.

References

[1] V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 169 (1993).

[2] K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

[5] NASA Evaluation No. 11, 1994 (see references in Introduction).

[6] R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, Science **252**, 693 (1991).

[7] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, K. Rothwell, and R. P. Wayne, Nature **347**, 541 (1990).

HO + CF_3Br(Halon 1301) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<4\times10^{-16}$	298	Orkin and Khamaganov, 1993[1]	(a)
$<4\times10^{-16}$	460		
Reviews and Evaluations			
$<1\times10^{-16}$	298	IUPAC, 1992[2]	(b)
$<1\times10^{-16}$	298	Atkinson, 1994[3]	(b)
$<1.2\times10^{-16}$	298	NASA, 1994[4]	(b)

Comments

(a) Discharge flow system with EPR detection of HO radicals.

(b) Based on the data of Burkholder *et al.*[5]

Preferred Values

$k<1\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit to the rate coefficient at 298 K is based on the upper limits to the rate coefficients of $<1\times10^{-16}$ cm^3 molecule^{-1} s^{-1} determined by Burkholder *et al.*[5] at 294 and 373 K, and is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 169 (1993).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).

HO + CF_2ClBr(Halon 1211) → products

No new data have been published since our last evaluation.

Preferred Values

$k<1\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit is based on the upper limits to the rate coefficients of $<1\times10^{-16}$ cm^3 molecule^{-1} s^{-1} determined by Burkholder *et al.*[1] at 297 and 373 K. The preferred value is consistent with the earlier study of Clyne and Holt,[2] and is identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).
[2] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 569 (1979).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + CF_2Br_2(Halon 1202) → products

No new data have been published since our last evaluation.

Preferred Values

$k<5\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit is based on the sole study of Burkholder *et al.*[1] The preferred upper limit to the rate coefficient at 298 K is confirmed by the values of $k\leq4\times10^{-16}$ cm^3 molecule^{-1} s^{-1} measured at 384 and 424 K,[1] and is identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CF_3CH_2Br$(Halon 2301) → $H_2O + CF_3CHBr$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Commen
Absolute Rate Coefficients			
8.5×10^{-13} exp[$-(1113\pm35)/T$]	298–460	Orkin and Khamaganov, 1993[1]	(a)
$(2.05\pm0.16)\times10^{-14}$	298		
1.39×10^{-12} exp[$-(1350\pm195)/T$]	280–353	Nelson, Zahniser, and Kolb, 1993[2]	(b)
$(1.45\pm0.13)\times10^{-14}$	294		
Reviews and Evaluations			
1.44×10^{-12} exp($-1337/T$)	280–460	Atkinson, 1994[3]	(c)

Comments

(a) Discharge flow system with EPR detection of HO radicals.

(b) Discharge flow system with LIF detection of HO radicals.

(c) Based on the absolute rate coefficients of Orkin and Khamaganov[1] and Nelson *et al.*[2]

Preferred Values

$k=1.6\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.4\times10^{-12}$ exp($-1335/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 280–460 K.

Reliability

$\Delta\log k=\pm0.20$ at 298 K.

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The rate coefficients of Nelson *et al.*[2] are ~15%–25 lower than those of Orkin and Khamaganov[1] over the ten perature range common to both studies (298–353 K). least-squares analysis of the rate coefficients of Orkin ar Khamaganov[1] and Nelson *et al.*[2] yields the preferred Arrhei ius expression.

References

[1] V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 169 (1993).

[2] D. D. Nelson, Jr., M. S. Zahniser, and C. E. Kolb, Geophys. Res. Lett. 2 197 (1993).

[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

$HO + CF_3CHFBr$(Halon 2401) → $H_2O + CF_3CFBr$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comme
Absolute Rate Coefficients			
7.2×10^{-13} exp[$-(1111\pm32)/T$]	298–460	Orkin and Khamaganov, 1993[1]	(a)
$(1.75\pm0.17)\times10^{-14}$	298		
Reviews and Evaluations			
1.1×10^{-12} exp($-1250/T$)	270–430	IUPAC, 1992[2]	(b)
8.09×10^{-13} exp($-1157/T$)	279–460	Atkinson, 1994[3]	(c)

Comments

(a) Discharge flow system with EPR detection of HO radicals.

(b) Based on the absolute rate coefficients of Brown *et al.*[4]

(c) Based on the absolute rate coefficients of Brown *et a* and Orkin and Khamaganov.[1]

Preferred Values

$k=1.7\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=8.1\times10^{-13}\exp(-1155/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 279–460 K.

Reliability

$\Delta\log k=\pm0.20$ at 298 K.
$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The absolute rate coefficients of Brown *et al.*[4] and Orkin and Khamaganov[1] are in good agreement. A least-squares analysis of the rate coefficients of Brown *et al.*[4] and Orkin and Khamaganov[1] yields the preferred values.

References

[1] V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 169 (1993).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[4] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, K. Rothwell, and R. P. Wayne, Nature **347**, 541 (1990).

HO + $CF_3CHClBr$(Halon 2311) → H_2O + CF_3CClBr

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.28\times10^{-12}\exp[-(995\pm38)/T]$	298–460	Orkin and Khamaganov, 1993[1]	(a)
$(4.50\pm0.40)\times10^{-14}$	298		
Reviews and Evaluations			
5.8×10^{-14}	298	IUPAC, 1992[2]	(b)
$1.2\times10^{-12}\exp(-970/T)$	298–460	Atkinson, 1994[3]	(c)

Comments

(a) Discharge flow system with EPR detection of HO radicals.
(b) Based on the absolute rate coefficient of Brown *et al.*[4]
(c) Based on the absolute rate coefficients of Orkin and Khamaganov.[1]

Preferred Values

$k=4.6\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=1.2\times10^{-12}\exp(-970/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 298–460 K.

Reliability

$\Delta\log k=\pm0.20$ at 298 K.
$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The rate coefficient of Brown *et al.*[4] at 303 K is ~25% higher than that calculated from the Arrhenius expression of Orkin and Khamaganov.[1] A least-squares analysis of the rate coefficients of Orkin and Khamaganov[1] leads to the preferred Arrhenius expression.

References

[1] V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 169 (1993).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[4] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

HO + CF_2BrCF_2Br(Halon 2402) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<4\times10^{-16}$	298	Orkin and Khamaganov, 1993[1]	(a)
$<4\times10^{-16}$	460		
Reviews and Evaluations			
$<1.3\times10^{-16}$	298	IUPAC, 1992[2]	(b)
$<1.5\times10^{-16}$	298	Atkinson, 1994[3]	(b)
$<1.5\times10^{-16}$	298	NASA, 1994[4]	(b)

Comments

(a) Discharge flow system with EPR detection of HO radicals.
(b) Based on the upper limits to the rate coefficients measured by Burkholder *et al.*[5]

Preferred Values

$k < 1.3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the study of Burkholder *et al.*[5] and is identical to our previous evaluation, IUPAC, 1992.[2] The upper limit to the rate coefficient at 374 K of $< 1.4 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} [5] confirms the upper limit observed at 298 K.

References

[1] V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 169 (1993).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).

$Br + NO_3 \rightarrow BrO + NO_2$

$\Delta H^\circ = -27$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.6 \pm 0.5) \times 10^{-11}$	298	Mellouki *et al.*, 1989[1]	(a)
Reviews and Evaluations			
1.6×10^{-11}	298	NASA, 1994[2]	(b)

Comments

(a) Discharge flow system. The decays of Br atoms in excess concentrations of the NO_3 radical were monitored by EPR. Computer simulations of the decays were carried out with a mechanism consisting of five reactions.
(b) Based on the results of Mellouki *et al.*[1]

Preferred Values

$k = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the room temperature results of Mellouki *et al.*[1] This study,[1] using the discharge flow-EPR technique, is the only experimental study of this reaction.

References

[1] A. Mellouki, G. Poulet, G. Le Bras, R. Singer, J. P. Burrows, and G. K. Moortgat, J. Phys. Chem. **93**, 8017 (1989).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).

$BrO + NO_3 \rightarrow BrOO + NO_2$

$\Delta H^\circ = -57$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(0.3\text{–}3.0) \times 10^{-12}$	298	Mellouki *et al.*, 1989[1]	(a)
Reviews and Evaluations			
1.0×10^{-12}	298	NASA, 1994[2]	(b)

Comments

(a) Discharge flow system. The decays of Br atoms and BrO radicals were monitored by EPR. Computer simulations of the results were carried out with a mechanism consisting of five reactions.
(b) Based on the results of Mellouki *et al.*[1]

Preferred Values

$k = 1.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred value is based on the room temperature results of Mellouki *et al.*[1] This study,[1] using the discharge flow-EPR technique, is the only experimental study of this reaction. The preferred value is the geometric mean of the upper and lower limits,[1] which are encompassed within the stated uncertainty factor. The Br-O_2 bond is very weak and the bond energy has been estimated by Blake *et al.*[3] to be 4 kJ mol^{-1}. Thus the product BrOO will quickly fall apart to yield Br + O_2.

References

[1] A. Mellouki, G. Poulet, G. Le Bras, R. Singer, J. P. Burrows, and G. K. Moortgat, J. Phys. Chem. **93**, 8017 (1989).
[2] NASA Evaluation No. 11, 1994 (see references in Introduction).
[3] J. A. Blake, R. J. Browne, and G. Burns, J. Chem. Phys. **53**, 3320 (1970).

$NO_3 + HBr \rightarrow HNO_3 + Br$

$\Delta H^\circ = -60.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<1 \times 10^{-16}$	298	Mellouki *et al.*, 1989[1]	(a)
$(1.3 \pm 1.1) \times 10^{-16}$	298	Canosa-Mas *et al.*, 1989[2]	(b)
Reviews and Evaluations			
$<1 \times 10^{-16}$	298	NASA, 1994[3]	(c)

Comments

(a) Discharge flow-EPR technique. Value derived from fitting the measured data to a complex mechanism.
(b) Discharge flow-multipath absorption technique. Value derived from fitting the measured data to a complex mechanism.
(c) Based on the results of Mellouki *et al.*[1]

Preferred Values

$k = <1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is the upper limit reported by Mellouki *et al.*[1] in a study using the discharge flow-EPR technique. Canosa-Mas *et al.*[2] reported a value derived from fitting their data to a complex mechanism which, within the stated uncertainty limits, is consistent with the upper limit reported by Mellouki *et al.*[1]

References

[1] A. Mellouki, G. Poulet, G. Le Bras, R. Singer, J. P. Burrows, and G. K. Moortgat, J. Phys. Chem. **93**, 8017 (1989).
[2] C. E. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **85**, 709 (1989).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$BrO + HO_2 \rightarrow HOBr + O_2$ (1)
$\rightarrow HBr + O_3$ (2)

$\Delta H^\circ(1) = -190\ kJ \cdot mol^{-1}$
$\Delta H^\circ(2) = -33\ kJ \cdot mol^{-1}$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.3 \pm 0.5) \times 10^{-11}$	298	Poulet *et al.*, 1992[1]	(a)
$(3.4 \pm 1.0) \times 10^{-11}$	298	Bridier, Veyret, and Lesclaux, 1993[2]	(b)
Reviews and Evaluations			
$6.2 \times 10^{-12} \exp(500/T)$	200–300	IUPAC, 1992[3]	(c)
$6.2 \times 10^{-12} \exp(500/T)$	200–300	NASA, 1994[4]	(d)

Comments

(a) Discharge flow system in which the pseudo-first-order decays of BrO in excess HO_2 were monitored by mass spectrometry.
(b) Flash photolysis/UV absorption technique.
(c) Based on the room temperature results of Poulet *et al.*[1] and an estimated temperature dependence.
(d) Based on the room temperature results of Poulet *et al.*[1] and Bridier *et al.*[2] and an estimated temperature dependence.

Preferred Values

$k = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.2 \times 10^{-12} \exp(500/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred value at 298 K is based on the recent study of Poulet *et al.*[1] in which BrO radical decays in excess HO_2 were monitored by DF/MS. This room temperature rate coefficient value is confirmed by the recent results of Bridier *et al.*[2] using a completely different technique. These new results are preferred over those reported in the earlier study of Cox and Sheppard[5] by molecular modulation-UV absorption in which a much lower value (by a factor of 6) was reported. The temperature dependence is our estimate, based on analogy with the ClO + HO_2 reaction. In the study of Poulet *et al.*,[1] the only product observed was HOBr. From a study of the reverse reaction at above room temperature, Mellouki *et al.*[6] have determined by extrapolation that the yield of HBr + O_3 is negligible (<0.01%) down to 200 K.

References

[1] G. Poulet, M. Pirre, F. Maguin, R. Ramaroson, and G. Le Bras, Geophys. Res. Lett. **19**, 2305 (1992).
[2] I. Bridier, B. Veyret, and R. Lesclaux, Chem. Phys. Lett. **201**, 563 (1993).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] R. A. Cox and D. W. Sheppard, J. Chem. Soc. Faraday Trans. 2, **78**, 1383 (1982).
[6] A. Mellouki, R. K. Talukdar, and C. J. Howard, J. Geophys. Res. **99**, 22949 (1994).

$BrO + O_3 \rightarrow Br + 2O_2$

$\Delta H^\circ = -156\ kJ \cdot mol^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$< 5 \times 10^{-17}$	298	Mauldin, Wahner, and Ravishankara, 1993[1]	(a)
Reviews and Evaluations			
$< 5 \times 10^{-15}$	298	IUPAC, 1992[2]	(b)
$< 1 \times 10^{-12} \exp(-3000/T)$	200–300	NASA, 1994[3]	(c)

Comments

(a) Flash photolysis-long path UV absorption technique. The upper limit was derived from an analysis of the [BrO] temporal profiles.
(b) Based on the results of Sander and Watson.[4]
(c) Based on the room temperature upper limit of Mauldin *et al.*[1] and an estimated *A*-factor.

Preferred Values

$k = <5\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit is based on the results reported by Mauldin *et al.*[1] As a result of improved sensitivity for detection of BrO, this upper limit is a factor of 100 less than that reported by Sander and Watson,[4] who carried out similar experiments. The 298 K value should also be a reasonably good upper limit for stratospheric temperatures.

References

[1] R. L. Mauldin III, A. Wahner, and A. R. Ravishankara, J. Phys. Chem. **97**, 7585 (1993).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] S. P. Sander and R. T. Watson, J. Phys. Chem. **85**, 4000 (1981).

$BrO + NO \rightarrow Br + NO_2$

$\Delta H^\circ = -70$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=2.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=8.7\times10^{-12}\exp(260/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 224–425 K.

Reliability

$\Delta\log k = \pm0.1$ at 298 K.
$\Delta(E/R) = \pm100$ K.

Comments on Preferred Values

The results of the three low pressure mass spectrometric studies[1–3] and the high pressure UV absorption study,[4] which all used pseudo-first-order conditions, are in excellent agreement at 298 K and are considered to be more reliable than the earlier low pressure UV absorption study of Clyne and Cruse.[5] The results of the two temperature dependence studies[3,4] are in good agreement. The preferred Arrhenius expression is derived from a least-squares fit to all the data in Refs. 1–4. By combining the data reported in the high pressure UV absorption study[4] with those from the mass spectrometric studies,[1–3] it can be shown that this reaction does not exhibit any observable pressure dependence between 1 mbar and 1 bar total pressure. The temperature dependences of the rate coefficient for the analogous ClO and HO_2 reactions are also negative and similar in magnitude. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[6]

References

[1] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **71**, 336 (1975).
[2] G. W. Ray and R. T. Watson, J. Phys. Chem. **85**, 2955 (1981).
[3] M. T. Leu, Chem. Phys. Lett. **61**, 275 (1979).
[4] R. T. Watson, S. P. Sander, and Y. L. Yung, J. Phys. Chem. **83**, 2936 (1979).
[5] M. A. A. Clyne and H. W. Cruse, Trans. Faraday Soc. **66**, 2227 (1970).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$BrO + NO_2 + M \rightarrow BrONO_2 + M$

$\Delta H° = -111$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
5.4×10^{-31} $(T/300)^{-3.2}$ [N$_2$]	248–346	Thorn, Daykin, and Wine, 1993[1]	(a)
Reviews and Evaluations			
4.7×10^{-31} $(T/300)^{-3.1}$ [N$_2$]	200–300	IUPAC, 1992[2]	(b)
5.2×10^{-31} $(T/300)^{-3.2}$ [air]	200–300	NASA, 1994[3]	(c)
1.7×10^{-30} [N$_2$]	200	Rayez and Destriau, 1993[4]	(d)
5.2×10^{-31} [N$_2$]	300		

Comments

(a) Photolysis of Br_2-NO_2-N_2 (or CF_4) mixtures at 351 nm. BrO was generated by the reaction $O(^3P) + Br_2 \rightarrow BrO + Br$ and monitored by absorption at 338.3 nm in a multipass system (up to 552 cm). Bath gas pressures were varied over the range 16–800 Torr. Data are based on an analysis with $F_c=\exp(-T/327)$. If a $F_c=0.6$ is used, a rate coefficient of $k_0=5.2\times10^{-31}$ $(T/300)^{-3.2}$ [N$_2$] cm^3 molecule^{-1} s^{-1} is obtained.

(b) Average of the data of Refs. 1 (preliminary version), 5, and 6 using $F_c=\exp(-T/327)$ for the falloff extrapolation.

(c) Recommended value was based on the values from Ref. 1, which are in excellent agreement with those of Ref. 5.

(d) Theoretical calculation[7] of k_0 using $\Delta H_0^\circ=135$ kJ mol^{-1} and $\beta_c=0.37$ and 0.28 at 200 K and 300 K, respectively. If $\Delta H_0^\circ=151$ kJ mol^{-1} is employed, β_c values of 0.16 and 0.12 are obtained at 200 K and 300 K, respectively.

Preferred Values

$k_0=4.7\times10^{-31}$ $(T/300)^{-3.1}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_0=\pm0.1$ at 298 K.

$\Delta n=\pm1$.

Comments on Preferred Values

The preferred values, which are based on data from Refs. 1, 5, and 6, are identical to our previous evaluation, IUPAC, 1992.[2]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.4×10^{-11} $(T/300)^{-1.2}$	248–346	Thorn, Daykin, and Wine, 1993[1]	(a)
Reviews and Evaluations			
1.7×10^{-11} $(T/298)^{-0.6}$	200–300	IUPAC, 1992[2]	(b)
6.9×10^{-12} $(T/300)^{-2.9}$	200–300	NASA, 1994[3]	(c)
4.0×10^{-12}	200	Rayez and Destriau, 1993[4]	(d)
5.0×10^{-12}	300		

Comments

(a) See comment (a) for k_0. If instead of $F_c=\exp(-T/327)$, a fixed value of $F_c=0.6$ is employed in fitting the falloff curves, a rate coefficient of $k_\infty=6.9\times10^{-12}$ $(T/300)^{-2.9}$ cm^3 molecule^{-1} s^{-1} is obtained.

(b) See comment (b) for k_0. A temperature-independent value would be also compatible with the available data.

(c) See comment (c) for k_0.

(d) Theoretical calculations[8] using $\Delta H_0^\circ=135$ kJ mol^{-1}. If $\Delta H_0^\circ=151$ kJ mol^{-1} is employed, $k_\infty=5.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} and 6.0×10^{-11} cm^3 molecule^{-1} s^{-1} are obtained at 200 K and 300 K, respectively.

Preferred Values

$k_\infty = 1.7 \times 10^{-11} (T/300)^{-0.6}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.1$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] R. P. Thorn, E. P. Daykin, and P. H. Wine, Int. J. Chem. Kinet. **25**, 521 (1993).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).
[3] NASA Evaluation No. 11, 1994 (see references in Introduction).
[4] M. T. Rayez and M. Destriau, Chem. Phys. Lett. **206**, 278 (1993).
[5] S. P. Sander, G. W. Ray, and R. T. Watson, J. Phys. Chem. **85**, 199 (1981).
[6] F. Danis, F. Caralp, J. Masanet, and R. Lesclaux, Chem. Phys. Lett. **167**, 450 (1990).
[7] J. Troe, J. Chem. Phys. **66**, 4758 (1977); J. Phys. Chem. **83**, 114 (1979).
[8] J. Troe, Z. Phys. Chem. NF **161**, 209 (1989).

$BrO + ClO \rightarrow Br + OClO$ (1)
$\rightarrow Br + ClOO$ (2)
$\rightarrow BrCl + O_2$ (3)

$\Delta H°(1) = -19$ kJ·mol^{-1}

$\Delta H°(2) = -17$ kJ·mol^{-1}

$\Delta H°(3) = -212$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k_1 = 6.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2 = 6.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_3 = 1.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 1.6 \times 10^{-12} \exp(430/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.

$k_2 = 2.9 \times 10^{-12} \exp(220/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.

$k_3 = 5.8 \times 10^{-13} \exp(170/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \Delta \log k_3 = \pm 0.1$ at 298 K.

$\Delta(E_1/R) = \Delta(E_2/R) = \Delta(E_3/R) = \pm 200$ K.

Comments on Preferred Values

In recent years there has been a substantial improvement in the data-base for this rate coefficient. Friedl and Sander,[1] using discharge flow-mass spectrometry techniques, measured the overall rate constant over the temperature range 220–400 K and also over this temperature range determined directly the branching ratios for the reaction channels producing BrCl and OClO. In a separate study the same authors, using flash photolysis-ultraviolet absorption techniques,[2] determined the overall rate constant over the temperature range 220–400 K and pressure range 50–750 Torr and also determined at 220 K and 298 K the branching ratio for OClO production. The results by these two independent techniques[1,2] are in excellent agreement, with the overall rate constant showing a negative temperature dependence. Toohey and Anderson,[3] using discharge flow-resonance fluorescence/LMR techniques, reported room temperature values of the overall rate constant and the branching ratio for OClO production. They also found evidence for the direct production of BrCl in a vibrationally excited π state. Poulet *et al.*,[4] using discharge flow-mass spectrometry techniques, reported room temperature values of the overall rate constant and branching ratios for OClO and BrCl production.

All the above-mentioned results[1–4] are in reasonably good agreement. Hills *et al.*,[5] using a discharge flow-mass spectrometry technique, obtained an overall rate constant which was independent of temperature over the range 241–308 K and substantially lower than the room temperature average of the above mentioned studies; they also reported no BrCl production. Room temperature overall rate constant values reported also include that from the discharge flow-mass spectrometry study of Clyne and Watson[6] and the very low value derived in the flash photolysis study of Basco and Dogra[7] using a different interpretation of the reaction mechanism. The recommended Arrhenius expressions for the individual reaction channels are taken from the study of Friedl and Sander.[1] That study[1] and the recent study of Turnipseed *et al.*[8] contain the most comprehensive sets of rate coefficient and branching ratio data. The overall rate coefficients reported in these two studies are in good agreement (within 20%) at room temperature and are in excellent agreement at stratospheric temperatures. Both of these studies, as well as that of Sander and Friedl,[2] show that OClO production by channel (1) becomes dominant at very low temperature. Both studies show an ~8% yield of BrCl by channel (3). The recommended expressions are consistent with the body of data from all studies except those of Refs. 5 and 7. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[9]

References

[1] R. R. Friedl and S. P. Sander, J. Phys. Chem. **93**, 4756 (1989).
[2] S. P. Sander and R. R. Friedl, J. Phys. Chem. **93**, 4764 (1989).
[3] D. W. Toohey and J. G. Anderson, J. Phys. Chem. **92**, 1705 (1988).
[4] G. Poulet, I. T. Lancar, G. Laverdet, and G. Le Bras, J. Phys. Chem. 94 278 (1990).
[5] A. J. Hills, R. J. Cicerone, J. G. Calvert, and J. W. Birks, J. Phys. Chem **92**, 1853 (1988).
[6] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, 73 1169 (1977).
[7] Basco and S. K. Dogra, Proc. Roy. Soc. London A, **323**, 417 (1971).
[8] A. A. Turnipseed, J. W. Birks, and J. G. Calvert, J. Phys. Chem. **95**, 435 (1991).
[9] IUPAC, Supplement IV, 1992 (see references in Introduction).

$BrO + BrO \rightarrow 2Br + O_2$ (1)
$\rightarrow Br_2 + O_2$ (2)

$\Delta H°(1) = -26$ kJ·mol^{-1}
$\Delta H°(2) = -219$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.75 \pm 0.57) \times 10^{-12}$	298	Mauldin, Wahner, and Ravishankara, 1993[1]	(a)
$k_2 = (4.45 \pm 0.82) \times 10^{-13}$	298		
$(3.1 \pm 0.4) \times 10^{-12}$	298	Bridier, Veyret, and Lesclaux, 1993[2]	(b)
Branching Ratios			
$k_1/k = 0.84 \pm 0.01$	298	Mauldin, Wahner, and Ravishankara, 1993[1]	(a)
$k_1/k = 0.68 \pm 0.05$	220		
Reviews and Evaluations			
$1.1 \times 10^{-12} \exp(250/T)$	223-400	IUPAC, 1992[3]	(c)
$k_1 = 2.1 \times 10^{-12}$	298		
$k_2 = 4.1 \times 10^{-13}$	298		
$k_1 = 4.0 \times 10^{-12} \exp(-190/T)$	200-300	NASA, 1994[4]	(d)
$k_2 = 4.2 \times 10^{-14} \exp(660/T)$	200-300		

Comments

(a) Flash photolysis/long path absorption technique. Measurements were made at 298 and 220 K over a pressure range of 75–600 Torr He, N_2, and SF_6. The overall rate coefficient was found to be independent of pressure at 298 K, but at 220 K to increase from 2.0×10^{-12} cm^3 molecule^{-1} s^{-1} at 100 Torr to 3.1×10^{-12} cm^3 molecule^{-1} s^{-1} at 400 Torr. The branching ratio was found to be independent of pressure at 298 K and 220 K. An additional, transient absorption feature was observed at 220 K and was tentatively attributed to Br_2O_2.

(b) Flash photolysis/UV absorption technique.

(c) Recommended Arrhenius expression for overall rate coefficient was based on the temperature dependent data of Sander and Watson[5] and Turnipseed *et al.*[6] and the room temperature data of Clyne and Watson[7] and Lancar *et al.*[8] The value of the branching ratio at room temperature was based on the data of Refs. 5, 6, 8–10.

(d) Recommended expressions for k_1 and k_2 were those proposed by Mauldin *et al.*[1] for atmospheric modeling.

Preferred Values

$k_1 = 2.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 3.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 4.0 \times 10^{-12} \exp(-190/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.
$k_2 = 4.2 \times 10^{-14} \exp(660/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.1$ at 298 K.
$\Delta (E_1/R) = \pm 150$ K.
$\Delta (E_2/R) = \pm 300$ K.

Comments on Preferred Values

The total rate coefficient for disappearance of BrO ($k = k_1 + k_2$) has been studied by a variety of techniques, including discharge flow-mass spectrometry (Clyne and Watson,[7] Turnipseed *et al.*,[6] and Lancar *et al.*[8]) and flash photolysis-ultraviolet absorption (Sander and Watson,[5] Bridier *et al.*,[2] and Mauldin *et al.*[1]).

The partitioning of the total rate coefficient into its two components, k_1 and k_2, has been measured at room temperature by Sander and Watson,[5] Turnipseed *et al.*,[6] and Lancar *et al.*,[8] by Jaffe and Mainquist[10] from 258 to 333 K, by Cox *et al.*[9] from 278 to 348 K, and by Mauldin *et al.*[1] from 220 to 298 K. All are in agreement that $k_1/k=0.85\pm0.03$ at 298 K. Mauldin *et al.*[1] reported the overall rate coefficient to be independent of pressure at 298 K but to increase with increasing pressure at 220 K. The recommended expressions for k_1 and k_2 are those proposed by Mauldin *et al.*[1] for atmospheric modeling. They are derived from an analysis of published data at pressures less than 100 Torr from the studies of Clyne and Watson,[7] Sander and Watson,[5] Turnipseed *et al.*,[6] and Mauldin *et al.*[1] They are consistent with an overall rate coefficient value of $(2.5\pm0.9)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature. They are based on values of $k_1/k=0.85$ at 298 K (all studies) and 0.68 at 220 K (Mauldin *et al.*[1] and Cox *et al.*,[9] extrapolated value). In the study of Mauldin *et al.*,[1] an additional, short-lived, absorption feature was observed at 220 K and was tentatively attributed to the dimer Br_2O_2.

References

[1] R. L. Mauldin, A. Wahner, and A. R. Ravishankara, J. Phys. Chem. **97**, 7585 (1993).

[2] I. Bridier, B. Veyret, and R. Lesclaux, Chem. Phys. Lett. **201**, 563 (1993).

[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

[4] NASA Evaluation No. 11, 1994 (see references in Introduction).

[5] S. P. Sander and R. T. Watson, J. Phys. Chem. **85**, 4000 (1981).

[6] A. A. Turnipseed, J. W. Birks, and J. G. Calvert, J. Phys. Chem. **94**, 7477 (1990).

[7] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **71**, 336 (1975).

[8] I. T. Lancar, G. Laverdet, G. Le Bras, and G. Poulet, Int. J. Chem. Kinet. **23**, 37 (1991).

[9] R. A. Cox, D. W. Sheppard, and M. P. Stevens, J. Photochem. **19**, 189 (1982).

[10] S. Jaffe and W. K. Mainquist, J. Phys. Chem. **84**, 3277 (1980).

$$CH_2BrO_2 + CH_2BrO_2 \rightarrow CH_2BrOOCH_2Br + O_2 \quad (1)$$

$$\rightarrow 2CH_2BrO + O_2 \quad (2)$$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq3.26\times10^{-11}$	298	Nielsen *et al.*, 1991[1]	(a,b)
Branching Ratios			
$k_2/k\approx1.0$	298	Nielsen *et al.*, 1991[1]	(c)
Reviews and Evaluations			
$k_{obs}=3.0\times10^{-11}$	298	Lightfoot *et al.*, 1992[2]	(d)

Comments

(a) k is defined by $-d[CH_2BrO_2]/dt=2k[CH_2BrO_2]^2$ and has been derived from the measured overall second-order decay of CH_2BrO_2 radicals (k_{obs}).

(b) Pulse radiolysis study of CH_3Br-O_2-SF_6 mixtures with CH_2BrO_2 radicals being monitored by UV absorption [$\sigma_{250}=(7.20\pm0.83)\times10^{-18}$ cm^2 molecule^{-1}]. The derived value of $k_{obs}=(3.26\pm0.31)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K, which was independent of wavelength over the range 250–310 nm and of pressure over the range 114–760 Torr of SF_6, is an upper limit to k because of the possibility of secondary reactions giving rise to an enhanced decay of CH_2BrO_2 radicals (see Comments on Preferred Values).

(c) CH_2BrO_2 radicals were generated from the steady-state photolysis of Cl_2 in the presence of CH_3Br-air mixtures. Two major carbon-containing products, CO and HCOBr, were observed by FTIR spectroscopic analysis.

(d) Based on the data of Nielsen *et al.*[1]

Preferred Values

$k\leq3.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k\leq1.0$ at 298 K.

Comments on Preferred Values

Following Lightfoot *et al.*,[2] we have recommended an upper limit to the overall rate coefficient at 298 K based on the results of Nielsen *et al.*[1] We note, however, that the absorption spectrum of the CH_2BrO_2 radical is surprisingly different from that of other published spectra of RO_2 radicals and this raises some uncertainty in the assignment.

The product study of Nielsen *et al.*[1] indicated the formation of HCOBr, which is assumed to arise from the reactionCH$_2$BrO + O$_2$ → HCOBr + HO$_2$. HCOBr was unstable and slowly decomposed to CO, the second major observed product. The absence of any CH$_2$BrOOBrCH$_2$ product indicates that reaction (1) is insignificant. The lack of detailed quantitative information on the branching ratio, k_2/k, and on the rate coefficient of the CH$_2$BrO$_2$ + HO$_2$ reaction precludes any correction of the loss of CH$_2$BrO$_2$ radicals by this route. Consequently, the experimental value to k_{obs} can only be taken as an upper limit value to k in the meantime.

It is interesting to note that the rate coefficient for the self-reaction of the CH$_2$BrO$_2$ radical is significantly greater than those observed for analogous reactions of any other alkyl peroxy radicals.

References

[1] O. J. Nielsen, J. Munk, G. Locke, and T. J. Wallington, J. Phys. Chem. **95**, 8714 (1991).

[2] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).

$$\mathrm{BrCH_2CH_2O_2 + BrCH_2CH_2O_2 \rightarrow BrCH_2CH_2OH + BrCH_2CHO + O_2} \quad (1)$$

$$\mathrm{\rightarrow 2BrCH_2CH_2O + O_2} \quad (2)$$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
3.9×10^{-12}	298	Crowley and Moortgat, 1992[1]	(a,b)
Branching Ratios			
$k_2/k=0.58$	298	Yarwood, Peng, and Niki, 1992[2]	(c)

Comments

(a) k is defined by $-d[\mathrm{BrCH_2CH_2O_2}]/dt = 2k[\mathrm{BrCH_2CH_2O_2}]^2$ and has been derived from the measured overall second-order decay of BrCH$_2$CH$_2$O$_2$ radicals (k_{obs}).

(b) Molecular modulation study of the photolysis of Br$_2$ in the presence of C$_2$H$_4$-O$_2$-N$_2$ mixtures at total pressures up to 600 Torr. BrCH$_2$CH$_2$O$_2$ radicals were monitored by absorption at 240 nm. The observed second-order decay of BrCH$_2$CH$_2$O$_2$ corresponded to $k_{obs}=(6.2\pm1.2)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K, from which the above value of k was derived by taking $k_2/k=0.58$.

(c) Steady-state photolysis of Br$_2$ in the presence of C$_2$H$_4$-O$_2$-N$_2$ mixtures at 700 Torr total pressure, with FTIR spectroscopic determination of products. The major products observed were BrCH$_2$CHO, BrCH$_2$CH$_2$OH, and BrCH$_2$CH$_2$OOH. The branching ratio, $k_2/k_1=1.35\pm0.07$, was determined from the yields of BrCH$_2$CHO and BrCH$_2$CH$_2$OH relative to the loss of C$_2$H$_4$.

Preferred Values

$k=3.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k=0.58$ at 298 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.
$\Delta(k_2/k)=\pm0.1$ at 298 K.

Comments on Preferred Values

The preferred value is derived from the measured value of k_{obs} determined by Crowley and Moortgat[1] and correcting for secondary removal of BrCH$_2$CH$_2$O$_2$ radicals by use of the branching ratio $k_2/k=0.58$ derived from the data of Yarwood *et al.*[2]

Confirmation of both k and k_2/k is needed, but the above value of k is consistent with the data for other halogenated alkyl peroxy radicals, which show enhanced self-reaction rate coefficients relative to the unsubstituted alkyl peroxy radicals.

References

[1] J. N. Crowley and G. K. Moortgat, J. Chem. Soc. Faraday Trans. **88**, 2437 (1992).

[2] G. Yarwood, N. Peng, and H. Niki, Int. J. Chem. Kinet. **24**, 369 (1992).

$BrO+CH_3SCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.65\pm0.65)\times10^{-13}$	298	Barnes *et al.*, 1989[1]	(a)
$(2.7\pm0.5)\times10^{-13}$	298	Barnes *et al.*, 1991[2]	(a)
Reviews and Evaluations			
2.7×10^{-13}	298	NASA, 1994[3]	(b)

Comments

(a) Fast flow discharge system used. BrO radicals were produced by the reaction $Br_2 + O \rightarrow BrO + Br$, and were monitored by mass spectrometry.

(b) Based on the rate coefficient of Barnes *et al.*[2]

Preferred Values

$k<2.7\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The two available measurements of the rate coefficient come from the same laboratory using basically the same technique.[1,2] In the earlier study of this reaction[1] and of the corresponding reaction of ClO with CH_3SCH_3, difficulties were encountered due to wall reactions. In this respect the later study[2] is much improved.

There is good agreement between the two results but measurements on the IO and ClO radical reactions with CH_3SCH_3 in the same study[2] gave values for the rate coefficients for these radicals reacting with CH_3SCH_3 some 30 times smaller than the reaction of BrO. In view of this unexpected difference and the difficulties associated with the measurements, it is suggested that the value of k obtained by Barnes *et al.*[2] be taken as an upper limit to k until further studies are made.

The reaction is usually assumed to produce $CH_3S(O)CH_3 + Br$ but, although the sulfoxide has been detected[1] as expected, no yields have been measured.

References

[1] I. Barnes, K. H. Becker, D. Martin, P. Carlier, G. Mouvier, J. L. Jourdain, G. Laverdet, and G. Le Bras, *Biogenic Sulfur in the Environment*, edited by E. S. Saltzman and W. J. Cooper, ACS Symposium Series, No. 393, p. 464 (1989).

[2] I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, Int. J. Chem. Kinet. **23**, 579 (1991).

[3] NASA Evaluation No. 11, 1994 (see references in Introduction).

$HOBr + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$HOBr + h\nu \rightarrow HO + Br$	(1)	201	595
$\rightarrow HBr + O(^3P)$	(2)	263	455
$\rightarrow BrO + H$	(3)	393	304

Absorption cross-section data

Wavelength range/nm	Reference	Comments
240–400	Orlando and Burkholder, 1995[1]	(a)

Comments

The absorption spectrum of HOBr was recorded using a diode-array spectrometer with a resolution of 0.4 nm. The spectrum consists of two bands, the stronger band peaking near 280 nm and a weaker band peaking near 350 nm. HOBr was prepared by the reaction of Br_2O with H_2O. The spectrum of Br_2O was also reported.

Preferred Values

Absorption cross-sections for photolysis of HOBr

λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$
240	0.43	320	3.9
245	1.9	325	4.2
250	4.5	330	4.9
255	8.2	335	5.3
260	12.9	340	5.7
265	18.5	345	6.0
270	24.0	350	6.0
275	28.5	355	5.9
280	30.8	360	5.7
285	30.4	365	5.2
290	27.3	370	4.5
295	22.3	375	3.8
300	16.4	380	3.0
305	11.0	385	2.2
310	7.0	390	1.7
315	4.8	395	1.1
		400	0.18

Comments on Preferred Values

The preferred cross-section values are from the recent study of Orlando and Burkholder.[1] This is the first reported study of the gas-phase UV/visible absorption spectrum. Previously, in the absence of experimental data for HOBr in the gas phase, it was suggested[2] that modelers use the recommended HOCl cross-section data redshifted by 30 nm. Using the new spectral data Orlando and Burkholder[1] calculated atmospheric photolysis rates to be significantly slower than those estimated previously. The new data yield a lifetime with respect to photolysis to be about 1 hour at ground level and about 0.5 hour in the lower stratosphere. By analogy with HOCl photolysis is expected to occur with unit quantum efficiency by breaking of the O-Br bond to yield HO + Br.

References

[1] J. J. Orlando and J. B. Burkholder, J. Phys. Chem. **99**, 1143 (1993).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

BrO + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{\mathrm{threshold}}$/nm
$BrO + h\nu \rightarrow Br + O(^3P)$ (1)	232	515
$\rightarrow Br + O(^1D)$ (2)	422	283

Preferred Values

Absorption cross-sections for BrO photolysis at 303 K

λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$
300–305	200	340–345	515
305–310	259	345–350	399
310–315	454	350–355	228
315–320	391	355–360	172
320–325	600	360–365	161
325–330	753	365–370	92
330–335	628	370–375	51
335–340	589		

Comments on Preferred Values

The BrO radical has a banded absorption spectrum in the 290–380 nm range. The absorption cross-section values at the band peaks are dependent on temperature and spectral resolution. The band locations, vibrational level assignments, and absorption cross-section values at 0.4 nm resolution are reported by Wahner *et al.*[1] The strongest absorption feature is the (7,0) band at 338.5 nm; the cross-section for 0.18 nm resolution was determined to be $(1.71\pm0.14)\times10^{-17}$ cm^2 at 298 K and $(2.21\pm0.16)\times10^{-17}$ cm^2 at 223 K.[1]

The preferred values given here are the averaged values over 5 nm intervals reported by Cox *et al.*;[2] in that paper the authors used these data to calculate a lifetime against solar photodissociation of 30 seconds for a solar zenith angle of 30 degrees. Earlier studies are discussed in previous evaluations.[3,4]

References

[1] A. Wahner, A. R. Ravishankara, S. P. Sander, and R. R. Friedl, Chem. Phys. Lett. **152**, 507 (1988).

[2] R. A. Cox, D. W. Sheppard, and M. P. Stevens, J. Photochem. **19**, 189 (1982).

[3] CODATA, 1980 (see references in Introduction).

[4] CODATA, Supplement II, 1984 (see references in Introduction).

$BrONO_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$BrONO_2 + h\nu \rightarrow BrO + NO_2$	(1)	111	1080
$\rightarrow Br + NO_3$	(2)	129	930
$\rightarrow BrONO + O(^3P)$	(3)	306	390
$\rightarrow BrONO + O(^1D)$	(4)	496	240

Preferred Values

Absorption cross-sections for $BrONO_2$ photolysis

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
186	1500	280	29
190	1300	285	27
195	1000	290	24
200	720	295	22
205	430	300	19
210	320	305	18
215	270	310	15
220	240	315	14
225	210	320	12
230	190	325	11
235	170	330	10
240	130	335	9.5
245	100	340	8.7
250	78	345	8.5
255	61	350	7.7
260	48	360	6.2
265	39	370	4.9
270	34	380	4.0
275	31	390	2.8

Quantum Yields

No recommendation is given for the relative importance of the possible pathways since there are no data which provide a basis for a recommendation.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1982.[1] The recommended values are taken from Spencer and Rowland.[2] They are unchanged from those given in CODATA, 1980,[3] where a detailed discussion can be found.

References

[1] CODATA, Supplement I, 1982 (see references in Introduction).
[2] J. E. Spencer and F. S. Rowland, J. Phys. Chem. **82**, 7 (1978).
[3] CODATA, 1980 (see references in Introduction).

$CH_3Br + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$CH_3Br + h\nu \rightarrow CH_3 + Br$	295	405

Preferred Values

Absorption cross-sections for CH_3Br photolysis at 298 K

λ/nm	$10^{20}\ \sigma/cm^2$	λ/nm	$10^{20}\ \sigma/cm^2$
190	44	230	15
2	53	2	12
4	62	4	9.9
6	69	6	7.6
8	76	8	5.9
200	79	240	4.5
2	80	2	3.3
4	79	4	2.5
6	77	6	1.8
8	73	8	1.3
210	67	250	0.96
2	61	2	0.69
4	56	4	0.49
6	49	6	0.34
8	44	8	0.23
220	38	260	0.16
2	32		
4	28		
6	23		
8	19		

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Gillotay and Simon.[1] Molina *et al.*[2] reported values at 5 nm intervals, and Robbins[3] reported values at 2 nm intervals. The agreement among these three studies[1–3] over the wavelength range of our preferred values is very good. The temperature dependence down to 210 K has been reported in Ref. 1. At shorter wavelengths the cross-section is independent of temperature,[1] while at $\lambda >$ 210 nm there is a decrease in absorption as the temperature is lowered.[1] For values at low temperatures the reader is referred to the original reference.[1] Photolysis has been shown by Talukdar *et al.*[4] to occur with unit quantum efficiency by breaking of the C-Br bond to yield CH_3 + Br.

References

[1] D. Gillotay and P. C. Simon, Annales Geophysicae. **6**, 211 (1988).
[2] L. T. Molina, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **86**, 2672 (1982).
[3] D. E. Robbins, Geophys. Res. Lett. **3**, 213 (1976).
[4] R. K. Talukdar, G. L. Vaghjiani, and A. R. Ravishankara, J. Chem. Phys. **96**, 8194 (1992).

CF_3Br (Halon-1301) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$CF_3Br + h\nu \rightarrow CH_3 + Br$	286	420

Preferred Values

Absorption cross-sections for CF_3Br photolysis at 298 K

λ/nm	$10^{20}\ \sigma/cm^2$	λ/nm	$10^{20}\ \sigma/cm^2$
190	6.4	230	3.1
2	7.5	2	2.4
4	8.5	4	1.9
6	9.5	6	1.4
8	10.4	8	1.1
200	11.2	240	0.81
2	11.8	2	0.59
4	12.2	4	0.43
6	12.4	6	0.31
8	12.4	8	0.22
210	12.0	250	0.16
2	11.4	2	0.11
4	10.7	4	0.076
6	9.8	6	0.053
8	8.8	8	0.037
220	7.7	260	0.026
2	6.7	2	0.018
4	5.7	4	0.012
6	4.7	6	0.009
8	3.8	8	0.006

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon[1] and Burkholder *et al.*[2] Molina *et al.*[3] reported values at 5 nm intervals. The agreement among these three studies[1–3] over the wavelength range of preferred values is excellent. The temperature dependence down to 210 K has been reported in Refs. 1 and 2. At $\lambda > 220$ nm both studies reported a decrease in absorption as the temperature is lowered.[1,2] Near the absorption peak (about 205 nm) Burkholder *et al.*[2] reported the cross-section to be independent of temperature, while Gillotay and Simon[1] found the absorption to increase with decreasing temperature, with a 20% increase at the lowest temperature studied. For values at low temperatures the reader is referred to the original references.[1,2] Photolysis has been shown by Talukdar *et al.*[4] to occur with unit quantum efficiency by breaking of the C-Br bond to yield CF_3 + Br. CF_3Br has no apparent tropospheric chemical loss mechanism[2] and is estimated to have a tropospheric lifetime against direct solar photoexcitation of greater than 1000 years.[3]

References

[1] D. Gillotay and P. C. Simon, J. Atmos. Chem. **8**, 41 (1989).

[2] J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).

[3] L. T. Molina, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **86**, 2672 (1982).

[4] R. K. Talukdar, G. L. Vaghjiani, and A. R. Ravishankara, J. Chem. Phys. **96**, 8194 (1992).

CF_2ClBr(Halon-1211) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$CF_2ClBr + h\nu \rightarrow CF_2Cl + Br$	271	440

Preferred Values

Absorption cross-sections for CF_2ClBr photolysis at 298 K

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²
190	47	240	18
2	15	2	15
4	70	4	12
6	83	6	10
8	96	8	8
200	112	250	6.5
2	118	2	5.1
4	121	4	4.0
6	122	6	3.2
8	121	8	2.4
210	117	260	1.9
2	112	2	1.4
4	106	4	1.1
6	98	6	0.84
8	90	8	0.63
220	81	270	0.48
2	72	2	0.36
4	64	4	0.27
6	56	6	0.20
8	49	8	0.15
230	42	280	0.11
2	36	2	0.079
4	31	4	0.058
6	26	6	0.043
8	22	8	0.031

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon[1] and Burkholder *et al.*[2] Molina *et al.*[3] reported values at 5 nm intervals, and Giolondo *et al.*[4] reported values at 10 nm intervals. The agreement among these four studies[1-4] over the wavelength range of our preferred values is excellent. The temperature dependence down to 210 K has been reported in Refs. 1 and 2. At $\lambda > 230$ nm both studies reported a decrease in absorption as the temperature is lowered.[1,2] Near the absorption peak (about 205 nm) Burkholder *et al.*[2] reported the cross-section to be independent of temperature, while Gillotay and Simon[1] found the absorption to increase with decreasing temperature reaching nearly a 20% increase at the lowest temperature. For values at low temperatures the reader is referred to the original references.[1,2] Over the wavelength range of the preferred values photolysis is expected to occur with unit quantum efficiency by breaking of the C-Br bond to yield CF_2Cl + Br. Baum and Huber,[5] in a photofragment translational spectroscopy study of the photodissociation of CF_2ClBr at 193 nm, found the dominant primary photodissociation process to occur by breaking of the C-Br bond and a second, minor process to occur by breaking of the stronger C-Cl bond. CF_2ClBr has been estimated to have a tropospheric lifetime against direct solar photoexcitation of 15 to 20 years.[2,3]

References

[1] D. Gillotay and P. C. Simon, J. Atmos. Chem. **8**, 41 (1989).

[2] J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).

[3] L. T. Molina, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **86**, 2672 (1982).

[4] D. M. Giolando, G. B. Fazekas, W. D. Taylor, and G. A. Takacs, J. Photochem. **14**, 335 (1980).

[5] G. Baum and J. R. Huber, Chem. Phys. Lett. **213**, 427 (1993).

CF_2Br_2(Halon-1202) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol⁻¹	$\lambda_{threshold}$/nm
$CF_2Br_2 + h\nu \rightarrow CF_2Br + Br$	280 (est)	430

Preferred Values

Absorption cross-sections for CF_2Br_2 photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	114	250	59
2	109	2	47
4	100	4	37
6	91	6	29
8	82	8	23
200	75	260	18
2	72	2	13
4	74	4	10
6	81	6	7.6
8	93	8	5.7
210	110	270	4.2
2	136	2	3.1
4	155	4	2.2
6	180	6	1.6
8	203	8	1.2
220	224	280	0.89
2	242	2	0.65
4	251	4	0.48
6	253	6	0.34
8	250	8	0.24
230	241	290	0.18
2	227	2	0.13
4	209	4	0.096
6	189	6	0.068
8	168	8	0.050
240	147	300	0.036
2	125	2	0.026
4	106	4	0.019
6	88	6	0.014
8	73	8	0.010

Quantum Yields

$\phi = 1.0$ throughout this wavelength range.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon[1] and Burkholder *et al.*[2] Molina *et al.*[3] reported values at 5 nm intervals. The agreement among these three studies[1–3] over the wavelength range of our preferred values is very good. The temperature dependence down to 210 K has been reported in Refs. 1 and 2, with fair agreement between the studies.[1,2] At λ>250 nm both studies reported a decrease in absorption as the temperature is lowered.[1,2] Near the absorption peak (about 230 nm) both studies report an 11% increase in absorption at the lowest temperature.[1,2] For values at low temperatures the reader is referred to the original references.[1,2] It has been shown by Molina and Molina[4] and confirmed by Talukdar *et al.*[5] that CF_2Br_2 photodissociates with unit quantum efficiency over the 200–300 nm region by breaking of the C-Br bond to yield CF_2Br + Br. Because its absorption extends into the 290–310 nm wavelength range, CF_2Br_2 has a short tropospheric lifetime against direct solar photoexcitation of about 3 years.[2]

References

[1] D. Gillotay and P. C. Simon, J. Atmos. Chem. **8**, 41 (1989).

[2] J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).

[3] L. T. Molina, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **86**, 2672 (1982).

[4] L. T. Molina and M. J. Molina, J. Phys. Chem. **87**, 1306 (1983).

[5] R. K. Talukdar, G. L. Vaghjiani, and A. R. Ravishankara, J. Chem. Phys. **96**, 8194 (1992).

$CHBr_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CHBr_3 + h\nu \rightarrow CHBr_2 + Br$	276	433

Preferred Values

Absorption cross-sections for $CHBr_3$ photolysis at 296 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	399	270	31
2	360	2	25
4	351	4	20
6	366	6	16
8	393	8	12
200	416	280	9.9
2	433	2	7.8
4	440	4	6.1
6	445	6	4.81
8	451	8	3.75
210	468	290	2.88
2	493	2	2.22
4	524	4	1.70
6	553	6	1.28
8	574	8	0.951
220	582	300	0.719
2	578	2	0.530
4	558	4	0.394
6	527	6	0.298
8	487	8	0.226
230	441	310	0.171
2	397	2	0.127
4	362	4	0.095
6	324	6	0.071
8	295	8	0.053
240	273	320	0.039
2	253	2	0.029
4	234	4	0.021
6	214	6	0.016
8	194	8	0.009
250	174	330	0.009
2	158	2	0.007
4	136	4	0.005
6	116	6	0.004
8	99	8	0.003
260	83	340	0.002
2	69		
4	57		
6	47		
8	38		

Comments on Preferred Values

There have been two studies of the absorption cross-sections of $CHBr_3$. Gillotay *et al.*[1] reported values over the wavelength range 170–310 nm and the temperature range 295–240 K; Moortgat *et al.*[2] reported values from 245–360 nm and the temperature range 296–256 K. In the region where the measurements overlap, the agreement is very good. The preferred values at room temperature are those reported by Gillotay *et al.*[1] over the wavelength range 190–284 nm and those reported by Moortgat *et al.*[2] at longer wavelengths. For values at lower temperatures, the following expression, $\ln \sigma(\lambda,T)=(0.06183-0.000241\ \lambda)\ (273-T)-(2.376+0.14757\ \lambda)$, was derived by Moortgat *et al.*[2] from a fit to the combined data of their study[2] and that of Gillotay *et al.*[1] It is valid for the wavelength range 290–340 nm and the temperature range 300–210 K. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Br bond to yield $CHBr_2$ + Br.

References

[1] D. Gillotay, A. Jenouvrier, B. Coquart, M. F. Merrienne, and P.C. Simon, Planet. Space Sci. **37**, 1127 (1989).

[2] G. K. Moortgat, R. Meller, and W. Schneider, in *The Tropospheric Chemistry of Ozone in the Polar Regions*, edited by H. Niki and K. H. Becker, NATO ASI Series, Volume 17 (Springer-Verlag, Berlin, 1993).

CF_2BrCF_2Br(Halon-2402) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{\mathrm{threshold}}$/nm
$CF_2BrCF_2Br + h\nu \rightarrow CF_2BrCF_2 + Br$	280 (est)	430

Preferred Values

Absorption cross-sections for CF_2BrCF_2Br photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	109	240	13
2	114	2	11
4	119	4	8.4
6	122	6	6.7
8	124	8	5.2
200	124	250	4.1
2	124	2	3.1
4	120	4	2.3
6	117	6	1.8
8	112	8	1.3
210	106	260	0.95
2	100	2	0.71
4	92	4	0.53
6	85	6	0.39
8	77	8	0.28
220	69	270	0.21
2	61	2	0.16
4	54	4	0.11
6	47	6	0.082
8	40	8	0.060
230	35	280	0.044
2	29		
4	24		
6	20		
8	16		

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay *et al.*[1] and Burkholder *et al.*[2] Molina *et al.*[3] have also reported values at 5 nm intervals. The agreement among these three studies over the wavelength range of preferred values is excellent. The temperature dependence down to 210 K has been reported in Refs. 1 and 2. The results differ qualitatively. For values at low temperatures the reader is referred to the original references.[1,2] Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Br bond to yield CF_2BrCF_2 + Br, and CF_2BrCF_2Br has been estimated to have a tropospheric lifetime against direct solar photoexcitation of 34 years.[2]

References

[1] D. Gillotay, P. C. Simon, and L. Dierickx, Aeronomica Acta **335**, 1 (1988).

[2] J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).

[3] L. T. Molina, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **86**, 2672 (1982).

4.9. Iodine Species

$O + I_2 \rightarrow IO + I$

$\Delta H° = -98$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 250$ K.

Comments on Preferred Values

The recommended rate coefficient is based on the data of Ray and Watson[1] and is consistent with the trend observed in the rate coefficients for the O + X_2 reaction, which increase steadily: $<1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} for X = F,[2] 4.2×10^{-14} cm^3 molecule^{-1} s^{-1} for X = Cl[3] and 1.4×10^{-11} cm^3 molecule^{-1} s^{-1} for X = Br[4] at 298 K. The molecular beam study of Parrish and Herschbach[5] suggests a zero activation energy, consistent with the near gas-kinetic value of k at 298 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[6]

References

[1] G. W. Ray and R. T. Watson, J. Phys. Chem. **85**, 2955 (1981).
[2] R. H. Krech, G. J. Diebold, and D. L. McFadden, J. Am. Chem. Soc. **99**, 4605 (1977).
[3] R. T. Watson, J. Phys. Chem. Ref. Data **6**, 871 (1977).
[4] IUPAC, Supplement III, 1989 (see references in Introduction).
[5] D. D. Parrish and D. R. Herschbach, J. Am. Chem. Soc. **95**, 6133 (1973).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).

$O + IO \rightarrow O_2 + I$

$\Delta H° = -249$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

This estimate is probably accurate to within a factor of 3, and is based upon the assumption that the reactivity of IO is similar to that of ClO and BrO (this is true in the case of XO + NO where X = F, Cl, Br, and I). The recommended rate constants for ClO and BrO at ~298 K are 3.8×10^{-11} cm^3 molecule^{-1} s^{-1} and 4.1×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively (see present evaluations). The temperature dependence of the rate constant is expected to be small. The preferred value is identical to that in our previous evaluation, IUPAC, 1992.[1]

References

[1] IUPAC, Supplement IV, 1992 (see references in Introduction).

$I + HO_2 \rightarrow HI + O_2$

$\Delta H° = -94.9$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 3.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.5 \times 10^{-11} \exp(-1090/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are based on the two experimental studies reported by Jenkin *et al.*,[1] which are the only reported measurements for this reaction. The rate coefficients k at 298 K agree quite well although both studies exhibited significant experimental error. The Arrhenius expression suggested by Jenkin *et al.*[1] is accepted for the temperature dependence. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.[2]

References

[1] M. E. Jenkin, R. A. Cox, A. Mellouki, G. Le Bras, and G. Poulet, J. Phys. Chem. **94**, 2927 (1990).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$I + O_3 \rightarrow IO + O_2$

$\Delta H° = -142$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=1.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=2.0\times10^{-11}\exp(-890/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–350 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The preferred Arrhenius expression uses the activation energy from Buben *et al.*[1] with an A factor adjusted to give the mean value at 298 K from the three studies of Buben *et al.*,[1] Jenkin and Cox,[2] and Sander.[3] The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] S. N. Buben, I. K. Larin, N. A. Messineva, and E. M. Trofimova, Khim. Fiz. **9**, 116 (1990).

[2] M. E. Jenkin and R. A. Cox, J. Phys. Chem. **89**, 192 (1985).

[3] S. P. Sander, J. Phys. Chem. **90**, 2194 (1986).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$I + NO + M \rightarrow INO + M$

$\Delta H° = -75.7$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k_0=1.8\times10^{-32}(T/300)^{-1.0}[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta\log k_0=\pm0.1$ at 300 K.

$\Delta n=\pm0.5$.

Comments on Preferred Values

The preferred values are based on the rate coefficients for M=Ar determined by van den Bergh *et al.*[1] and Basco and Hunt,[2] which agree remarkably well. The collision efficiencies for He, Ar, and N_2 follow the usual trends. The transition to the high pressure limit is of no importance for pressures below 1 bar ($k_\infty=1.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K, $F_c=0.75$ at 298 K, see Ref. 3). The preferred values are identical to those in our previous evaluation, IUPAC, 1992.[4]

References

[1] H. van den Bergh, N. Benoit-Guyot, and J. Troe, Int. J. Chem. Kinet. **9**, 223 (1977).

[2] N. Basco and J. E. Hunt, Int. J. Chem. Kinet. **10**, 733 (1978).

[3] CODATA, Supplement I, 1982 (see references in Introduction).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$I + NO_2 + M \rightarrow INO_2 + M$

$\Delta H° = -79.8$ kJ·mol^{-1}

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0=3.0\times10^{-31}\ (T/300)^{-1}\ [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta\log k_0=\pm0.2$ at 298 K.

$\Delta n=\pm1$.

Comments on Preferred Values

The preferred values are from Refs. 1–3. The data of Ref 4 for M=He are also consistent with the data of Refs. 1–3. Falloff extrapolations are made with a fitted[1] $F_c=0.63$ near 300 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty=6.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta\log k_\infty=\pm0.3$ over the temperature range 200–400 K.

Comments on Preferred Values

See comments on k_0. The preferred values for k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.[5]

References

[1] H. van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).
[2] H. van den Bergh, N. Benoit-Guyot, and J. Troe, Int. J. Chem. Kinet. 9, 223 (1977).
[3] S. N. Buben, I. K. Larin, N. A. Messineva, and E. M. Trofimova, Kin. i Kataliz **31**, 973 (1990).
[4] A. Mellouki, G. Laverdet, J. L. Jourdain, and G. Poulet, Int. J. Chem. Kinet. **21**, 1161 (1989).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$I + NO_3 \rightarrow IO + NO_2$

$\Delta H^\circ=-40$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.5\pm1.9)\times10^{-10}$	298	Chambers, Heard, and Wayne, 1992[1]	(a)

Comments

(a) Discharge flow system with resonance fluorescence detection of I atoms. NO_3 radicals were measured by visible absorption spectroscopy. The $O + I_2$ reaction was used to generate I atoms and NO_3 radicals were produced by the reaction $F + HNO_3$. Pseudo-first-order conditions were used with NO_3 in excess. Correction of k^1 of up to 33% was applied to compensate for diffusion effects; the overall error takes into account the uncertainties in $[NO_3]$ (26%) and k^1 (15% at the 95% confidence limits).

Preferred Values

No recommendation.

Comments on Preferred Values

This is a new data sheet. The only reported measurement of this rate constant was made using the discharge flow technique at room temperature.[1] Some difficulties were encountered due to wall reactions, and the pseudo first-order plots exhibited pronounced curvature at contact times longer than 3 ms. Lancar *et al.*[2] state that they failed to observe a reaction between I atoms and NO_3 radicals. In view of these uncertainties, no recommendation for the rate coefficient is made at this time.

References

[1] R. M. Chambers, A. C. Heard, and R. P. Wayne, J. Phys. Chem. **96**, 3321 (1992).
[2] I. T. Lancar, A. Mellouki, and G. Poulet, Chem. Phys. Lett. **177**, 554 (1991).

$I_2 + NO_3 \rightarrow I + IONO_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.5) \times 10^{-12}$	292–423	Chambers, Heard, and Wayne, 1992[1]	(a)

Comments

(a) Discharge flow system with simultaneous fluorescence detection of I_2 and visible absorption spectroscopic measurement of NO_3 radicals. NO_3 radicals were produced by the $F + HNO_3$ reaction. Pseudo-first-order conditions were used with NO_3 radical concentrations in excess over I_2. Experiments were performed to substantiate that I_2 loss was due to reaction with NO_3 radicals. Correction of k^1 of up to 2% was applied to compensate for diffusion effects; the overall error takes into account the uncertainties in $[NO_3]$ (26%).

Preferred Values

$k = 1.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–450 K.

Reliability

$\Delta \log k = \pm 0.3$.

Comments on Preferred Values

This is a new data sheet. The only reported measurement of this rate constant[1] was made using the discharge flow technique and is the basis of the recommended value. Thermochemical data give a substantial endothermicity for $XONO_2$ formation in the reactions of the other halogens with the NO_3 radical, and the rapid rate of the $I_2 + NO_3$ reaction implies an upper limit of ~29 kJ mol^{-1} for $\Delta H°$ $(IONO_2)$. Other possible channels giving $I + IO + NO_2$, $I + O_2 + INO$ or $IO + INO_2$ are all apparently endothermic.

References

[1] R. M. Chambers, A. C. Heard, and R. P. Wayne, J. Phys. Chem. **96**, 3321 (1992).

$HO + HI \rightarrow H_2O + I$

$\Delta H° = -200.9$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 3.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the results of Mac Leod *et al.*[1] and Lancar *et al.*,[2] which are more than a factor of two higher than the earlier results of Takacs and Glass.[3] The preferred value is identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] H. Mac Leod, C. Balestra, J. L. Jourdain, G. Laverdet, and G. Le Bras, Int. J. Chem. Kinet. **22**, 1167 (1990).

[2] I. T. Lancar, A. Mellouki, and G. Poulet, Chem. Phys. Lett. **177**, 554 (1991).

[3] G. A. Takacs and G. P. Glass, J. Phys. Chem. **77**, 1948 (1973).

[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + I_2 \rightarrow HOI + I$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The two reported values of Loewenstein and Anderson[1] and Jenkin *et al.*[2] agree well, considering the quoted error limits. The preferred value is the mean of these two studies,[1,2] and is identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] L. M. Loewenstein and J. G. Anderson, J. Phys. Chem. **89**, 5371 (1985).
[2] M. E. Jenkin, K. C. Clemitshaw, and R. A. Cox, J. Chem. Soc. Faraday Trans. 2, **80**, 1633 (1984).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CH_3I \rightarrow H_2O + CH_2I$

$\Delta H^\circ = -65.2$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k=7.2\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=3.1\times10^{-12}\exp(-1120/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–430 K.

Reliability

$\Delta\log k = \pm0.5$ at 298 K.

$\Delta(E/R) = \pm500$ K.

Comments on Preferred Values

The preferred rate coefficients are based on the sole study of Brown *et al.*,[1] and are identical to our previous evaluation, IUPAC, 1992.[2] The uncertainty limits in the preferred values take into account the significant error limits (±30–50% except at 298 K) cited by Brown *et al.*[1]

References

[1] A. C. Brown, C. E. Canosa-Mas, and R. P. Wayne, Atmos. Environ. **24A**, 361 (1990).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$HO + CF_3I \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.2\pm0.2)\times10^{-13}$	295	Garraway and Donovan, 1979[1]	(a)
$(3.1\pm0.5)\times10^{-14}$	300	Brown *et al.*, 1990[2]	(b)

Comments

(a) Flash photolysis system with resonance absorption detection of HO radicals.

(b) Discharge flow system with resonance fluorescence detection of HO radicals. The stated purity level of the CF_3I used was >97%.

Preferred Values

$k<4\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

In view of the potential for secondary reactions, reactions with impurities and/or heterogeneous wall reactions[3] in the study of Brown *et al.*[2] (which yields a significantly lower rate coefficient than obtained by Garraway and Donovan[1]), the rate coefficient obtained by Brown *et al.*[2] is taken as an upper limit value.

References

[1] J. Garraway and R. J. Donovan, J. Chem. Soc., Chem. Comm. 1108 (1979).
[2] A. C. Brown, C. E. Canosa-Mas, and R. P. Wayne, Atmos. Environ. **24A**, 361 (1990).
[3] R. P. Wayne, C. E. Canosa-Mas, A. C. Heard, and A. D. Parr, Atmos. Environ. **26A**, 2371 (1992).

$NO_3 + HI \rightarrow HNO_3 + I$

$\Delta H° = -128.6$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

No recommendation.

Comments on Preferred Values

Although the rate coefficients measured in the single study[1] of this reaction from the decay of NO_3 using MS and I atom production using EPR spectrometry were in agreement, there is a serious potential for secondary chemistry occurring in the system leading to an overestimation of the rate coefficient for the elementary process. The authors state that the reaction of $I + NO_3 \rightarrow IO + NO_2$ does not occur,[1] while Chambers *et al.*[2] observed that this $I + NO_3$ reaction is extremely rapid, with a rate coefficient of $k(I + NO_3) = 4.5\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K, and that I atoms are regenerated from subsequent reactions of IO. While this uncertainty exists, no recommendation can be made.

References

[1] I. T. Lancar, A. Mellouki, and G. Poulet, Chem. Phys. Lett. **177**, 554 (1991).

[2] R. M. Chambers, A. C. Heard, and R. P. Wayne, J. Phys. Chem. **96**, 3321 (1992).

$IO + HO_2 \rightarrow HOI + O_2$

$\Delta H° = -212$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.03\pm0.13)\times10^{-10}$	298	Maguin *et al.*, 1992[1]	(a)
Reviews and Evaluations			
6.4×10^{-11}	298	IUPAC, 1992[2]	(b)

Comments

(a) Discharge flow system with MS detection of HO_2 and IO radicals and HOI. IO radicals were produced by the reaction of $O(^3P)$ atoms with I_2 and HO_2 radicals by the reaction $Cl + CH_3OH + O_2$. Psuedo-first-order decays of IO radicals were measured in the presence of excess HO_2. The k value is the average of 28 experiments. HOI was shown to be a major product. The uniqueness of channel (1) could not be established, although no evidence was found for ozone formation by the alternative channel of $IO + HO_2 \rightarrow HI + O_3$.

(b) Based on the measurements of Jenkin *et al.*[3]

Preferred Values

$k=1.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.3$.

Comments on Preferred Values

The new study by Maguin *et al.*[1] provides a more direct determination of this rate coefficient than the earlier measurement[3] using the molecular modulation technique, which required computer simulations to derive the rate coefficient from the observed concentration-time profiles of IO and HO_2 radicals. The preferred value is therefore based on the more recent study,[1] which also provides strong evidence that HOI is the major product. On the basis of current thermochemical data for the IO radical, the channel forming $HI + O_3$ is endothermic by 47.6 kJ mol^{-1}. The value of k at 298 K is consistent with the emerging reactivity pattern for the halogen oxide radicals with the HO_2 radical. The temperature dependence is expected to be small.

References

[1] F. Maguin, G. Laverdet, G. Le Bras, and G. Poulet, J. Phys. Chem. **96**, 1775 (1992).

[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] M. E. Jenkin, R. A. Cox, and G. D. Hayman, Chem. Phys. Lett. **177**, 272 (1991).

$IO + IO \rightarrow I_2 + O_2$ (1)
$\rightarrow 2I + O_2$ (2)
$\rightarrow I + OIO$ (3)
$IO + IO + M \rightarrow I_2O_2 + M$ (4)

$\Delta H°(1) = -152$ kJ·mol^{-1}
$\Delta H°(2) = -0.5$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4$ [M])

No new data have been published since our last evaluation.

Preferred Values

$k = 5.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.7 \times 10^{-12} \exp(1020/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–373 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The most recent data of Barnes *et al.*[1] confirm that the pressure independence of the rate of this reaction, observed by Sander,[2] extends to low pressures as indicated by the less reliable results of Martin *et al.*[3] No new data relating to the branching ratios have been reported and therefore no recommendation can be made. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, Int. J. Chem. Kinet. **23**, 579 (1991).
[2] S. P. Sander, J. Phys. Chem. **90**, 2194 (1986).
[3] D. Martin, J. L. Jourdain, G. Laverdet, and G. Le Bras, Int. J. Chem. Kinet. **19**, 503 (1987).
[4] IUPAC, Supplement III, 1989 (see references in Introduction).

$IO + NO \rightarrow I + NO_2$

$\Delta H° = -57$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.3 \times 10^{-12} \exp(330/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The studies of Buben *et al.*[1] and Daykin and Wine[2] give values of k at 298 K midway between those reported in earlier studies.[3,4] The preferred value at 298 K is the mean of the values reported in Refs. 1–4. The temperature dependence measurements of Daykin and Wine[2] appear to be of excellent quality and provide the basis for the recommendation, which uses the preferred 298 K value with the E/R from Daykin and Wine.[2] The preferred values are identical to our previous evaluation, IUPAC, 1992.[5]

References

[1] S. N. Buben, I. K. Larin, N. A. Messineva, and E. M. Trofimova, in press (1995).
[2] E. P. Daykin and P. H. Wine, J. Phys. Chem. **94**, 4528 (1990).
[3] G. Inoue, M. Suzuki, and N. Washida, J. Chem. Phys. **79**, 4730 (1983).
[4] G. W. Ray and R. T. Watson, J. Phys. Chem. **85**, 2955 (1981).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

$IO + NO_2 + M \rightarrow IONO_2 + M$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.6\pm1.0)\times10^{-31}$ [He]	298	Maguin *et al.*, 1992[1]	(a)
$(7.9\pm2.2)\times10^{-31}$ [N_2]	298		
Reviews and Evaluations			
7.7×10^{-31} $(T/300)^{-5}$ [N_2]	250–350	IUPAC, 1992[2]	(b)
7.7×10^{-31} [N_2]	300	Rayez and Destriau, 1993[3]	(c)
5.9×10^{-31} $(T/300)^{-3.5}$ [N_2]	200–300	NASA, 1994[4]	(d)

Comments

(a) Discharge-flow study with detection of IO and $IONO_2$ by mass spectrometry. IO radicals were generated by the reaction $O + I_2 \rightarrow IO + I$. The pressure range was 1.2–2.1 Torr of He. Using a relative third-body efficiency of N_2 and He for the analogous reaction $BrO + NO_2 + M$ [ratio k_0 $(N_2)/k_0$ (He)=2.2] from Ref. 5, the value reported above was derived.

(b) Based on Ref. 6, with falloff extrapolations being made with $F_c=0.4$.

(c) Theoretical evaluation[7] of k_0 using $\Delta H_0^\circ=121$ kJ mol^{-1} and $\beta_c=0.73$. If $\Delta H_0^\circ=147$ kJ mol^{-1} is employed, a value of $\beta_c=0.17$ is obtained.

(d) Based on the data from Ref. 6.

Preferred Values

$k_0=7.7\times10^{-31}$ $(T/300)^{-5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability

$\Delta\log k_0=\pm0.3$ at 298 K.

$\Delta n=\pm2$.

Comments on Preferred Values

The value of Maguin *et al.*,[1] derived with the given ratio of efficiencies for N_2 and He, agrees very well with the previous preferred values,[2] which remain unchanged.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
1.6×10^{-11}	250–350	IUPAC, 1992[2]	(a)
6.0×10^{-12}	300	Rayez and Destriau, 1993[3]	(b)
9.0×10^{-12} $(T/300)^{-1.5}$	200–300	NASA, 1994[4]	(c)

Comments

(a) The preferred values were based on the data of Refs. 6 and 8. Falloff extrapolations were made with $F_c=0.4$ at 300 K.

(b) Theoretical calculations[9] using a $\Delta H_0^\circ=121$ kJ mol^{-1}. If $\Delta H_0^\circ=147$ kJ mol^{-1} is employed, a rate coefficient of $k_\infty=8.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} results.

(c) See comment (d) for k_0.

Preferred Values

$k_\infty=1.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–350 K.

Reliability

$\Delta\log k_\infty=\pm0.3$ over the temperature range 250–350 K.

Comments on Preferred Values

The preferred value for k_∞ is unchanged from our previous evaluation, IUPAC, 1992.[2]

References

[1] F. Maguin, G. Laverdet, G. Le Bras, and G. Poulet, J. Phys. Chem. 96, 1775 (1992).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

[3] M. T. Rayez and M. Destriau, Chem. Phys. Lett. **206**, 278 (1993).
[4] NASA Evaluation No. 11, 1994 (see references in Introduction).
[5] S. P. Sander, G. W. Ray, and R. T. Watson, J. Phys. Chem. **85**, 199 (1981).
[6] E. P. Daykin and P. H. Wine, J. Phys. Chem. **94**, 4528 (1990).
[7] J. Troe, J. Chem. Phys. **66**, 4758 (1977); J. Phys. Chem. **83**, 114 (197
[8] M. E. Jenkin and R. A. Cox, J. Phys. Chem. **89**, 192 (1985).
[9] J. Troe, Z. Phys. Chem. NF **161**, 209 (1989).

IO + $CH_3SCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Commen
Absolute Rate Coefficients			
$(3.0\pm1.5)\times10^{-11}$	296	Barnes *et al.*, 1987[1]	(a)
$(1.5\pm0.5)\times10^{-11}$	298	Martin *et al.*, 1987[2]	(b)
$<3.5\times10^{-14}$	298	Daykin and Wine, 1990[3]	(c)
$(1.5\pm0.2)\times10^{-14}$	298	Maguin *et al.*, 1991[4]	(d)
$(8.8\pm2.1)\times10^{-15}$	298	Barnes *et al.*, 1991[5]	(d)
Reviews and Evaluations			
1.2×10^{-14}	298	IUPAC, 1992[6]	(e)
1.2×10^{-14}	298	NASA, 1994[7]	(e)

Comments

(a) Photolysis of NO_2-I_2-CH_3SCH_3-N_2 mixtures. Photolytic production of $O(^3P)$ atoms from NO_2 gives IO via $O(^3P) + I_2 \rightarrow IO + I$ reaction. Concentrations of NO, NO_2, CH_3SCH_3, and CH_3SOCH_3 were followed as a function of time by FTIR. A computer fit of product yields to reaction mechanism gave k.

(b) Fast flow discharge system. IO radicals were produced by the reaction $O(^3P) + I_2 \rightarrow IO + I$. He carrier gas at approximately 1 Torr. CH_3SCH_3 consumption was monitored by mass spectrometry under second-order conditions.

(c) Pulsed laser photolysis of NO_2-I_2-CH_3SCH_3-N_2-O_2 mixtures at 351 nm. [IO] was monitored by long-path length absorption at 471 nm. Slow flow conditions used.

(d) Fast-flow discharge study. IO radicals were produced by the reaction $O(^3P) + I_2 \rightarrow IO + I$. Total pressure was "a few Torr" of He. [IO] was monitored by mass spectrometry.

(e) Derived from the rate coefficients of Maguin *et al.*[4] and Barnes *et al.*,[5] which are consistent with the upper limit to the rate coefficient measured by Daykin and Wine.[3]

Preferred Values

$k = 1.2\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.5$ at 298 K.

Comments on Preferred Values

In the earlier studies of this reaction by Barnes *et al.*[1] and Martin *et al.*,[2] erroneously high values were obtained which are now believed to have been due to features of the secondary chemistry and heterogeneous processes occurring under the conditions used.

The two most recent studies,[4,5] both using the same technique, give much lower values but differ from each other by nearly a factor of two. Support for these lower values comes from the study by Daykin and Wine[3] where an upper limit to k was obtained.

The preferred value of k is the mean of the values found by Maguin *et al.*[4] and Barnes *et al.*,[5] but in view of the differences between the results from these studies substantial error limits are assigned. The preferred value is identical to our previous evaluation, IUPAC, 1992.[6]

The reaction products are usually assumed to be $CH_3S(O)CH_3$ + I. $CH_3S(O)CH_3$ has been detected in a number of studies,[1,2,4,5] and a semi-quantitative measurement of the yield by Barnes *et al.*[5] gives 84±40%.

References

[1] I. Barnes, K. H. Becker, P. Carlier, and G. Mouvier, Int. J. Chem. Kinet. **19**, 489 (1987).
[2] D. Martin, J. L. Jourdain, G. Laverdet, and G. Le Bras, Int. J. Chem. Kinet. **19**, 503 (1987).
[3] E. P. Daykin and P. H. Wine, J. Geophys. Res. **95**, 18547 (1990).
[4] F. Maguin, A. Mellouki, G. Laverdet, G. Poulet, and G. Le Bras, Int. J. Chem. Kinet. **23**, 237 (1991).
[5] I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, Int. J. Chem. Kinet. **23**, 579 (1991).
[6] IUPAC, Supplement IV, 1992 (see references in Introduction).
[7] NASA Evaluation No. 11, 1994 (see references in Introduction).

$INO + INO \rightarrow I_2 + 2NO$

$\Delta H^\circ = 0.3$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 1.3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.4 \times 10^{-11} \exp(-2620/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–450 K.

Reliability

$\Delta \log k = \pm 0.4$ at 298 K.

$\Delta(E/R) = \pm 600$ K.

Comments on Preferred Values

The results from the study of Van den Bergh and Troe[1] are preferred over those from Basco and Hunt[2] because of a much wider range of conditions studied. The preferred values are identical to our previous evaluation, IUPAC, 1992.[3]

References

[1] H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).
[2] N. Basco and J. E. Hunt, Int. J. Chem. Kinet. **10**, 733 (1978).
[3] IUPAC, Supplement IV, 1992 (see references in Introduction).

$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$

$\Delta H^\circ = 8.4$ kJ·mol^{-1}

No new data have been published since our last evaluation.

Preferred Values

$k = 4.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.9 \times 10^{-11} \exp(-2600/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 298–400 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values

The preferred values are based on the measured rate constant at 350 K from Van den Bergh and Troe[1] and an assumed value for E/R equal to that for the reaction INO + INO → I_2 + 2NO. In the analogous reactions for other halogens this behavior appears to apply (see Ref. 1). The preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

$CH_2IO_2 + CH_2IO_2 \rightarrow CH_2IOH + HCOI + O_2$ (1)

$\rightarrow 2CH_2IO + O_2$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\sim 9 \times 10^{-11}$	295	Sehested, Ellermann, and Nielsen, 1994[1]	(a)

Comments

(a) Pulse radiolysis UV absorption spectrometric study of CH_3I-O_2-SF_6 mixtures at a total pressure of 1000 mbar. CH_2IO_2 radicals were monitored by UV absorption with $\sigma_{370} = (2.1 \pm 0.5) \times 10^{-18}$ cm^2 molecule^{-1}. The interpretation of the kinetic data is complicated by the presence of CH_3O_2 radicals, which leads to mixed-order kinetics. The above approximate value of k was derived on the basis of several assumptions.

Preferred Values

No recommendation.

Comments on Preferred Values

The approximate and exceptionally large rate coefficient obtained by Sehested *et al.*[1] should be regarded with caution owing to the inherent complications in their experimental system. Until more work is carried out in this reaction, we make no recommendation.

References

[1] J. Sehested, T. Ellermann, and O. J. Nielsen, Int. J. Chem. Kinet. **26**, 25 (1994).

HOI + $h\nu \rightarrow$ products

No new data have been published since our last evaluation.

Primary photochemical processes

Reactions		$\Delta H°$/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
HOI + $h\nu \rightarrow$ HO + I	(1)	236	507
$\rightarrow$ HI + O(^{3}P)	(2)	366	327
$\rightarrow$ IO + H	(3)	415	288
$\rightarrow$ HI + O(^{1}D)	(4)	555	216

Preferred Values

Absorption cross-sections of HOI at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
300–305	0.02	385–390	11.8
305–310	3.29	390–395	14.0
310–315	5.80	395–400	16.7
315–320	9.10	400–405	20.0
320–325	12.9	405–410	22.8
325–330	17.0	410–415	23.3
330–335	20.6	415–420	21.9
335–340	21.4	420–425	19.2
340–345	19.5	425–430	16.2
345–350	16.7	430–435	13.5
350–355	14.3	435–440	11.0
355–360	12.4	440–445	9.10
360–365	11.0	445–450	7.50
365–370	10.2	450–455	5.80
370–375	9.90	455–460	4.11
375–380	9.90	460–465	2.47
380–385	10.4	465–470	1.10
		470–475	0.28

Quantum Yields

No recommendation. Reaction (1) is the most likely pathway for photolysis in the lower atmosphere.

Comments on Preferred Values

The recommended values for the cross-sections are those given by Jenkin,[1] which are the only available data for the gas phase. Confirmation of these data are required. The preferred values are identical to our previous evaluation, IUPAC, 1992.[2]

References

[1] M. E. Jenkin, Ph.D Thesis, University of East Anglia (1991).
[2] IUPAC, Supplement IV, 1992 (see references in Introduction).

IO + $h\nu \rightarrow$ products

No new data have been published since our last evaluation.

Primary photochemical processes

Reactions		$\Delta H°$/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
IO + $h\nu \rightarrow$ I + O(^{3}P)	(1)	249	480
$\rightarrow$ I + O(^{1}D)	(2)	439	270

Preferred Values

Absorption cross-sections

λ/nm	10^{18} σ/cm^2	λ/nm	10^{18} σ/cm^2
415–420	8.4	445–450	14.1
420–425	9.3	450–455	4.0
425–430	16.4	455–460	10.0
430–435	2.9	460–465	4.2
435–440	10.2	465–470	2.8
440–445	3.1		

Temperature dependence of the IO absorption cross-section at 427.2 nm

Temp./K	10^{17} σ/cm^2
250	5.3±0.5
273	4.3±0.4
298	3.1±0.3
317	2.3±0.2
341	2.3±0.2
373	2.1±0.2

Comments on Preferred Values

Sander,[1] Stickel *et al.*,[2] and Cox and Coker[3] all report the same value of $\sigma=3.1\times10^{-17}$ cm^2 molecule^{-1} for the 4-0 band at a resolution of 0.27 nm or less. The preferred absorption cross-sections at 298 K are based on this value.

The preferred values, which are averaged over 5 nm intervals, are based on the data reported by Cox and Coker.[3] Stickel *et al.*[2] pointed out an error in Table II of Ref. 3 where the listed σ values averaged over 5 nm are a factor of 10 higher than the true values based on the data plotted in Figure 1 of that work. The atmospheric photolysis rate calculated from the tabulated data for a solar zenith angle of 40° (i.e., 0.3 s^{-1}) is consequently a factor of 10 too high. Stickel *et al.*[2] do not present averaged cross-section data, so it is not possible to utilize their measurements over the whole spectral range.

Sander[1] reported cross-sections at the head of the 4-0 band measured at six temperatures in the range 250–373 K. A strong temperature dependence is apparent at temperatures <317 K, with σ increasing with decreasing temperature.

No recommendation is given for the quantum yield. Durie and Ramsay[4] report extensive predissociation in the *A-X* progression of IO; therefore the quantum yield for process (1) is probably unity throughout the wavelength region of the preferred σ values.

The preferred values are identical to our previous evaluation, IUPAC, 1992.[5]

References

[1] S. P. Sander, J. Phys. Chem. **90**, 2194 (1986).
[2] R. E. Stickel, A. J. Hynes, J. D. Bradshaw, W. L. Chameides, and D. D. Davis, J. Phys. Chem. **92**, 1862 (1988).
[3] R. A. Cox and G. B. Coker, J. Phys. Chem. **87**, 4478 (1983).
[4] R. A. Durie and D. A. Ramsay, Can. J. Phys. **36**, 35 (1958).
[5] IUPAC, Supplement IV, 1992 (see references in Introduction).

INO + *hν* → products

No new data have been published since our last evaluation.

Primary photochemical transitions

Reactions	ΔH° /kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
INO + $h\nu$ → I + NO	76	1570

Preferred Values

Absorption cross-sections of INO at 298 K

λ/nm	$10^{17}\ \sigma/\mathrm{cm}^2$	λ/nm	$10^{17}\ \sigma/\mathrm{cm}^2$
230	1.4	380	0.065
235	5.3	390	0.078
238	7.0	400	0.92
245	6.5	410	1.10
251	5.9	420	0.10
260	2.4	430	0.094
270	1.0	440	0.080
300	0.09	450	0.060
360	0.045	460	0.040
370	0.059		

Comments on Preferred Values

The absorption cross-section values are the averages from the data of Refs. 1–3. The deviations between the results of these studies are only small. No quantum yield data are available. Presumably the photolysis quantum yield is unity over the whole wavelength range. The preferred values are identical to our previous evaluation, IUPAC, 1992.[4]

References

[1] H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).
[2] N. Basco and J. E. Hunt, Int. J. Chem. Kinet. **10**, 733 (1978).
[3] E. Forte, H. Hippler, and H. Van den Bergh, Int. J. Chem. Kinet. **13**, 1227 (1981).
[4] IUPAC, Supplement IV, 1992 (see references in Introduction).

$INO_2 + h\nu \rightarrow$ products

No new data have been published since our last evaluation.

Primary photochemical processes

Reactions	$\Delta H^\circ/\mathrm{kJ \cdot mol^{-1}}$	$\lambda_{\mathrm{threshold}}/\mathrm{nm}$
$INO_2 + h\nu \rightarrow I + NO_2$	80	1500

Absorption cross-section data

No absorption spectrum has been detected to date, although the spectrum has been searched for in the NO_2-catalyzed recombination of iodine atoms.[1] It is presumed that $\sigma(INO_2) < \sigma(NO_2)$ over the wavelength range 250–600 nm.

References

[1] H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).

$IONO_2 + h\nu \rightarrow$ products

No new data have been published since our last evaluation.

Primary photochemical processes

Reactions		$\Delta H^\circ/\mathrm{kJ \cdot mol^{-1}}$	$\lambda_{\mathrm{threshold}}/\mathrm{nm}$
$IONO_2 + h\nu \rightarrow IO + NO_2$	(1)		
$\rightarrow I + NO_3$	(2)		
$\rightarrow IONO + O(^3P)$	(3)		
$\rightarrow IONO + O(^1D)$	(4)		

Note: There are no thermodynamic data for $IONO_2$.

Absorption cross-section data

No experimental data are available.

Quantum yield data

No experimental data are available.

Preferred Values

Neither qualitative absorption spectra or absolute cross sections have been measured for $IONO_2$. It is suggested that in the absence of experimental data the absorption cross-section data for $BrONO_2$ be used (this will probably lead to an underestimate of the $IONO_2$ photolysis rate J as the $IONO_2$ spectrum is expected to be red-shifted relative to the $BrONO_2$ spectrum by ~50 nm).

$CH_3I + h\nu \rightarrow$ products

Primary photochemical processes

Reactions	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3I + h\nu \rightarrow CH_3 + I(^2P_{3/2})$	239	500
$\rightarrow CH_3 + I^*(^2P_{1/2})$	330	362

Absorption cross-section data

Wavelength range/nm	Reference	Comments
205–335	Jenkin *et al.*, 1993[1]	(a)
160–335	Fahr, Nayak, and Kurylo, 1995[2]	(b)

Comments

(a) The absorption spectrum of CH_3I was recorded using a diode array spectrometer with a resolution of approximately 1 nm using a purified sample. The absolute cross-section at the maximum of absorption at 257.9 nm was $\sigma = 1.22 \times 10^{-18}$ cm^2 molecule^{-1}.

(b) Absorption spectrum was measured over the temperature range 223–333 K. In addition to the gas-phase measurements over the wavelength range 160–335 nm, liquid-phase measurements over the range 330–400 nm were also reported. The liquid-phase values were converted into accurate gas-phase values at long wavelengths. The spectral resolution was approximately 0.1 nm. Cross-section values were reported at 0.5 nm intervals.

Preferred Values

Absorption cross-sections for CH_3I photolysis at 295 K, 253 K, and 223 K

	10^{20} σ/cm^2				10^{20} σ/cm^2		
λ/nm	295 K	253 K	223 K	λ/nm	295 K	253 K	223 K
220	6.87	6.06	6.39	290	8.71	7.01	5.83
225	9.09	8.46	8.56	295	4.15	3.18	2.69
230	12.7	11.5	11.9	300	2.09	1.57	1.34
235	20.8	19.8	19.9	305	1.11	0.84	0.75
240	39.1	37.4	37.7	310	0.62	0.49	0.44
245	69.4	67.9	69.0	315	0.37	0.29	0.27
250	105.7	104.9	108.4	320	0.24	0.20	0.16
255	133.9	134.9	140.1	325	0.13	0.11	–
260	138.8	140.9	148.5	330	0.067	0.055	–
265	119.8	120.2	123.9	335	0.039	0.032	–
270	87.2	86.1	87.2	340	0.020	0.020	–
275	56.1	52.9	52.2	345	0.010	0.010	–
280	32.8	31.0	26.9	350	0.005	0.005	–
285	16.7	14.4	12.9	355	0.005	0.003	–
				360	0.003	0.001	–

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Fahr *et al.*[2] These authors[2] reported measurements in the gas phase (160–335 nm) and the liquid phase (330–400 nm) over the temperature range 223-333 K. For the range of preferred values given here (220–360 nm), values were reported at 0.5 nm intervals.[2] A wavelength-shift procedure was used to convert the liquid-phase values into accurate gas-phase values at the long wavelengths.[2] Near the band maximum at 258.5 nm the cross-sections increased slightly (less than 15%) with a decrease in temperature.[2] For wavelengths greater than 275 nm the cross-sections decreased with a decrease in temperature.[2] The room temperature values reported in Ref. 2 are in good agreement (5–10%) with those reported by Jenkin *et al.*[1] for the wavelength regions $\lambda<245$ nm and $\lambda>280$ nm, but are 10–15% higher in the region of strongest absorption (250–270 nm). Other earlier room temperature results[3,4] appear to be in reasonably good agreement with the preferred values. No other studies of the temperature dependence of the UV absorption cross-section have been reported.

Photolysis is expected to occur with unit quantum yield by breaking of the C-I bond to yield CH_3 + I. Photodissociation is known to produce both ground state iodine atoms and iodine atoms in the $I^*(^2P_{1/2})$ excited state lying 91 kJ mol^{-1} above the ground state. Flash photolysis of CH_3I was the source of the first $I^*(^2P_{1/2} \rightarrow {}^2P_{3/2})$ laser at 1.315 μm.[5] The quantum yield for production of $I^*(^2P_{1/2})$ atoms has been shown to be strongly dependent on the photodissociation wavelength; for example, Baughcum and Leone[4] report that the value of $\phi(I^*)$ decreases from 0.81 at 248 nm to 0.05 at 308 nm.

References

[1] M. E. Jenkin, T. P. Murrells, S. J. Shalliker, and G. D. Hayman, J. Chem. Soc. Faraday Trans. **89**, 433 (1993).
[2] A. Fahr, A. K. Nayak, and M. J. Kurylo, Chem. Phys. **197**, 195 (1995).
[3] D. Porrett and C. F. Goodeve, Trans. Faraday Soc. **33**, 690 (1937).
[4] S. L. Baughcum and S. R. Leone, J. Chem. Phys. **72**, 6531 (1980).
[5] J. V. V. Kasper and G. C. Pimentel, Appl. Phys. Lett. **5**, 231 (1964).

$CF_3I + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_3I + h\nu \rightarrow CF_3 + I$	228	525

Preferred Values

Absorption cross sections for CF_3I photolysis at 298 K[a]

λ/nm	10^{20} σ/cm^2	10^3 B/K^{-1}
240	13.7	0.58
245	21.9	0.28
250	33.4	-0.04
255	46.9	-0.36
260	59.5	-0.61
265	66.9	-0.70
270	66.5	-0.57
275	59.0	-0.17
280	47.0	0.52
285	34.8	1.5
290	23.6	2.7
295	14.8	3.8
300	8.9	4.9
305	5.2	6.0
310	2.9	6.8
315	1.6	7.3
320	0.93	7.5
325	0.50	7.7
330	0.27	7.9
335	0.15	8.2
340	0.08	8.5
345	0.04	8.3

[a] Temperature dependence given by the expression: $\log_e\sigma = \log_e\sigma(298) + B(T-298)$ where T is temperature (K).

Absorption cross-section values have been reported by Solomon *et al.*[1] over the wavelength range 216–370 nm at 298 K and over the range 216–344 nm for T = 200–298 K; and by Fahr *et al.*[2] over the wavelength range 160–240 nm for temperatures 240, 295, and 355 K and over the range 240–350 nm for T = 218–333 K. The preferred values at 298 K are the average of the values reported by Solomon *et al.*[1] and by Fahr *et al.*[2] Results of these studies are in very good agreement at room temperature and agree to better than 15% at all temperatures. The temperature coefficient B values are those tabulated in Solomon *et al.*[1] At the longer wavelengths the cross-section values decrease significantly at lower temperatures; at 320 nm the value decreases by nearly 50% at 200 K. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-I bond to yield CF_3 + I.

References

[1] S. Solomon, J. B. Burkholder, A. R. Ravishankara, and R. R. Garcia, J. Geophys. Res. **99**, 20929 (1994).
[2] A. Fahr, A. K. Nayak, and R. E. Huie, Chem. Phys. **199**, 275 (1995).

5. HETEROGENEOUS REACTIONS

5.1. Introduction

Heterogeneous reactions taking place on surfaces of atmospheric particulates are now recognized to be important in the polar stratosphere of the southern as well as the northern hemisphere. Furthermore, heterogeneous processes occurring on sulfate/sulfuric acid aerosols in the stratosphere, under both background as well as volcanically enhanced conditions, are believed to be involved in the perturbed ozone chemistry observed in these situations. In addition, it is becoming increasingly clear that significant heterogeneous processes also take place in the free troposphere on atmospheric particulates related to emissions from air traffic. The assessment of the importance of heterogeneous chemical reactions taking place on surfaces of particulates present in the troposphere is an area of ongoing studies.

Heterogeneous reactions taking place at the gas-solid or gas-liquid interface are complex in contrast to the gas-phase rate processes presented in this compilation which involve elementary reactions. The primary experimental observable in a heterogeneous system is the rate of uptake of a trace gas species and in some cases the rate of formation of one or several product species. The uptake kinetics are often described in terms of the uptake coefficient, γ, a dimensionless parameter describing the probability that a gas phase species is removed irreversibly from the gas phase owing to the presence of an active surface in relation to the total number of gas-surface collisions with that surface. The uptake coefficient is defined in terms of the following equations depending upon whether the rate law for adsorption of the gas species is known or not:

$$\gamma=\frac{4R_{\mathrm{up}}}{\langle c\rangle n_g}$$

$$\gamma=\frac{k_{\mathrm{up}}}{\omega}\quad\text{where}\quad\omega=\frac{\langle c\rangle}{4V}$$

R_{up} and k_{up} are the experimentally determined uptake rate and rate coefficient, respectively, $\langle c\rangle$ is the average molecular speed of the gas, n_{g} is the concentration of the molecular species in the gas phase, ω is the gas-surface collision frequency in s^{-1} and V is the volume of the reaction vessel.

The observable rate of uptake of a species by a surface is a complex process and depends on several elementary processes such as gas-phase diffusion towards the surface of interest, the mass accommodation rate, the desorption rate from the surface back to the gas phase, the chemical transformation at the interface, the diffusion into the bulk of the condensed phase and possible chemical reactions within the bulk phase. The accommodation coefficient (α) describing the rate of mass accommodation relates to an elementary process and is not normally accessible to direct measurement or observation. The uptake coefficient γ refers to a series of processes and has therefore to be corrected for the various contributions in order to obtain information on α. A number of experiments are performed under conditions such that some or all of the contributions to γ vanish except those from α. In this case the uptake coefficient can be interpreted as a mass accommodation coefficient.

This evaluation concentrates on the presentation of kinetic data for the uptake of atmospheric trace gas species onto a condensed phase, i.e., uptake and accommodation coefficients. We have not included data from the older literature on heterogeneous reaction kinetics when it was clear that the results are at variance with most of the more recent conclusions. Conspicuously absent from our evaluations are Henry's law solubilities governing the uptake of trace gases into the fluid condensed phase and isotherms controlling the adsorption of gases onto solids. It is intended to include these data in a future evaluation. The standard reaction enthalpy and entropy changes have only been listed in selected cases where the condensed phase has been sufficiently well characterized.

The uptake coefficient or reaction probability γ listed in the Tables is presented in a variety of forms depending upon the experimental technique used:

- γ_{ss} describes an experimentally determined uptake coefficient obtained from measurements at steady state even though the physical state of the system may change fairly rapidly with time, for instance due to surface saturation. Several uptake experiments of flowing gases on solid surfaces are conducted at very low trace gas concentrations in order to avoid surface saturation. In this case the measured uptake coefficient will approximate to the mass accommodation coefficient.
- γ_0 corresponds to an experimentally determined initial uptake coefficient that was changing rapidly with time. This value may have been obtained either through extrapolation of time-dependent γ values or it corresponds to an uptake coefficient resulting from a pulsed experiment. In cases without additional complications, γ_0 may approach the mass accommodation coefficient.
- γ corresponds to an uptake coefficient that was processed or corrected through major algebraic manipulations such as corrections for gas-phase diffusion, liquid-phase saturation in relation to limiting Henry's law solubilities, and condensed-phase diffusion. This value often corresponds to the mass accommodation coefficient.
- γ_{obs}, γ_{max} correspond to the observed value of the uptake coefficient under defined experimental conditions and to its maximum value, respectively.
- γ_{X} corresponds to the uptake coefficient of species X in cases where more than one gas phase species has been exposed to the surface of interest.

For mixtures of H_2SO_4-H_2O, HNO_3-H_2O, and ternary mixtures containing HCl the composition is given in weight percent (%H_2SO_4, %HNO_3, %HCl), the concentrations are given in mol dm^{-3}; rh means relative humidity in percent based on the partial pressure of H_2O, $p(H_2O)$, even when solid substrates other than pure water ice are used and is calculated from:

$$\mathrm{rh}(\%)=100\,p(\mathrm{H_2O})/p_{\mathrm{ice}}(T/\mathrm{K}),$$

where $p_{ice}(T/K)$ corresponds to the vapor pressure of ice at temperature T(K). In some cases experimental results are listed without explicit knowledge of the nature and composition of the substrate. NAT, NAD, NAM, and SAT mean nitric acid trihydrate ($HNO_3 \cdot 3H_2O$), nitric acid dihydrate ($HNO_3 \cdot 2H_2O$), nitric acid monohydrate ($HNO_3 \cdot H_2O$), and sulfuric acid tetrahydrate ($H_2SO_4 \cdot 4H_2O$), respectively. Additional hydrates are listed by name rather than by their acronyms. The abbreviations used in the experimental descriptions are defined in the Guide to the Data Sheets for the Thermal Reactions.

The effect of surface porosities on the uptake kinetics of trace gases on "porous" surfaces such as ice and NaCl is not yet well defined. The term porosity implies that the sample in question is presented with significant interstitial void such as a powder or a rough condensed film rather than having pores on the molecular scale. One school of thought prepares substrates that are as smooth as possible to demonstrate the lack of a dependence of the measured kinetic results upon the substrate thickness. Another approach applies correction factors to the measured uptake coefficients ranging from a factor of four to sixteen, making the "true" uptake coefficient smaller than the measured one. It seems that the dependence of the uptake coefficient on the substrate porosity is observed for some gases (N_2O_5, $ClONO_2$) and not for others (H_2O, HNO_3).

Excluded from the present work are papers dealing with solubility-limited uptake experiments and their time-dependent uptake coefficients. These references will be compiled and evaluated in a future edition, which will also include Henry's law constants of importance to atmospheric chemistry.

5.2. Heterogeneous Reactions—Data Sheets

5.2.1. Uptake Kinetics with Chemical Reaction

$N_2O_5 + H_2O \rightarrow 2HNO_3$

(including uptake studies)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
	Sulfate/H_2SO_4 (liquid) Substrates				
γ_{ss}	$(4.9 \pm 0.7) \times 10^{-2}$	NH_4HSO_4 aerosol, 45–75% rh	293	Mozurkewich and Calvert, 1988[1]	(a)
	$(8.5 \pm 1.9) \times 10^{-2}$	NH_4HSO_4 aerosol, 55–75% rh	274		
	$(1.0 \pm 0.1) \times 10^{-1}$	H_2SO_4 aerosol, 1–10% rh	293		
	$(1.39 \pm 0.09) \times 10^{-1}$	H_2SO_4 aerosol, 1–10% rh	274		
γ_{ss}	$(1.2 \pm 0.3) \times 10^{-1}$	40% H_2SO_4	225.5	Hanson and Ravishankara, 1991[2]	(b)
	$(1.4 \pm 0.3) \times 10^{-1}$	60% H_2SO_4	225.5		
	$(1.0 \pm 0.2) \times 10^{-1}$	70% H_2SO_4	225.5		
	$(1.0 \pm 0.2) \times 10^{-1}$	75% H_2SO_4	225.5		
γ	$(5.8 \pm 0.6) \times 10^{-2}$	73% H_2SO_4 droplets	283	Van Doren *et al.*, 1991[3]	(c)
γ_{ss}	$(5.5 \pm 1.0) \times 10^{-2}$	74%–96% H_2SO_4	220±5	Golden *et al.*, 1992[4]; Williams *et al.*, 1994[5]; Manion *et al.*, 1994[6]	(d)
γ_{ss}	$(6 \pm 4) \times 10^{-2}$	78.7%–83.6% H_2SO_4	293	Fried *et al.*, 1994[7]	(e)
	$(1.03 \pm 0.06) \times 10^{-1}$	64.0%–81.4% H_2SO_4	273		
	$(1.20 \pm 0.16) \times 10^{-1}$	56.6%–76.2% H_2SO_4	260		
	$(1.48 \pm 0.11) \times 10^{-1}$	63.2%–76.0% H_2SO_4	247		
	$(0.86 \pm 0.09) \times 10^{-1}$	60.7%–62.1% H_2SO_4	247		
	$(1.46 \pm 0.36) \times 10^{-1}$	68.6%–70.9% H_2SO_4	230–234		
	$(1.02 \pm 0.11) \times 10^{-1}$	64.5%–68.6% H_2SO_4	231–234		
	$(0.77 \pm 0.19) \times 10^{-1}$	54.0%–63.7% H_2SO_4	225–231		
	Sulfate/H_2SO_4 (solid) Substrates				
γ_{ss}	$5.0 \times 10^{-3} < \gamma < 8.0 \times 10^{-3}$	57.5% H_2SO_4	195–205	Hanson and Ravishankara, 1993[8]	(f)
	$2.4 \times 10^{-3} < \gamma < 5.0 \times 10^{-3}$	60% H_2SO_4	192–205		
	HNO_3–H_2O Substrates				
γ_{max}	$(1.3 \pm 0.3) \times 10^{-2}$	bulk NAT	188	Quinlan *et al.*, 1990[9]	(g)
γ_{ss}	$(6 \pm 3) \times 10^{-4}$	NAT film	200	Hanson and Ravishankara, 1991[10]	(h)
γ_{ss}	6×10^{-4}	NAT	191	Hanson and Ravishankara, 1992[11]	(i)
γ_{ss}	$(3 \pm 1) \times 10^{-4}$	NAT	191	Hanson and Ravishankara, 1993[12]	(j)
γ_0	$\leqslant 1 \times 10^{-4}$	NAT film	160–205	Kenner, Ryan, and Plumb, 1994[13]	(k)
	H_2O (solid) Substrates				
γ_{ss}	$\geqslant 1.0 \times 10^{-3}$ (±50%)	ice film	185	Tolbert, Rossi, and Golden, 1988[14]	(l)
γ_{ss}	$(2.8 \pm 1.1) \times 10^{-2}$	ice film	195	Leu, 1988[15]	(m)
γ_{max}	$(3.4 \pm 0.8) \times 10^{-2}$	bulk ice	188	Quinlan *et al.*, 1990[9]	(n)
	$(2.3 \pm 0.8) \times 10^{-2}$	ice film	188		

(including uptake studies)—Continued

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$(2.4\pm0.8)\times10^{-2}$	ice film	200	Hanson and Ravishankara, 1991[10]	(h)
γ_{ss}	1.3×10^{-2}	ice film	191	Hanson and Ravishankara, 1992[11], 1993[12]	(i,j)
γ_0	$\geq1.0\times10^{-2}$	ice film	160–205	Kenner, Ryan, and Plumb, 1994[13]	(k)
	H_2O (liquid) Substrates				
γ	$(4.0\pm0.5)\times10^{-2}$	H_2O droplets	282	Van Doren *et al.*, 1990[16]	(o)
	$(6.1\pm0.4)\times10^{-2}$	H_2O droplets	271		
γ	$5.0\times10^{-3}\leq\gamma\leq1.0\times10^{-2}$	liquid jet	293.1	Kirchner *et al.*, 1990[17]	(p)
γ	$(3.0\pm0.2)\times10^{-2}$	H_2O droplets	262	George *et al.*, 1994[18]	(q)
	$(1.3\pm0.8)\times10^{-2}$	H_2O droplets	277		
	Other Substrates				
γ	3.0×10^{-3}	charcoal	300	Brouwer, Rossi, and Golden, 1986[19]	(r)
	5.0×10^{-3}	charcoal + H_2O	300		

Comments

(a) Uptake experiment in high-pressure (0.8 atm) flow tube using slow-flow conditions and fine size-selected aerosol. Three size classes in the range between 40–100 nm diameter were used in the uptake experiments. The maximum number density of 2.5×10^5 particles cm^{-3} was observed at 40 nm diameter. The value for the uptake coefficient was weakly dependent (increasing) on aerosol size in the range indicated and within experimental error. The significant value of γ_{ss} below the deliquescence point (rh $\leq$40%) is explained by evaporation of NH_3 and generation of a water-containing H_2SO_4 layer. By increasing the NH_4^+ content by 25%, γ_{ss} decreases at low and high rh. No significant uptake of N_2O_5 on $(NH_4)_2SO_4$ aerosol was observed at rh =25% at 293 K owing to the absence of a liquid layer on the aerosol surface. At 60% rh, γ_{ss} was measured as $(4.3\pm0.5)\times10^{-2}$. The uptake of N_2O_5 on H_2SO_4-H_2O was independent on rh in the range 1–10%. The negative temperature dependence of γ_{ss} observed throughout this work is interpreted in terms of increasing reevaporation of N_2O_5 with increasing temperature.

(b) Uptake experiment on a wetted-wall flow tube with chemical ionization MS detection. This method allows selective detection of N_2O_5 in the presence of HNO_3 and other reactants at characteristic densities of 10^{10} to 10^{11} molecule cm^{-3}. The cold aqueous solution of H_2SO_4 (40–75%, T=215–230 K) was flowing down the walls of the flow tube with a liquid film residence time of 20–30 s. $p(H_2O)$ was generally around 1 mTorr. Owing to diffusion limitations a correction had to be applied to γ taking into account the estimated diffusion coefficients of N_2O_5 in He. The temperature dependence of γ was measured for the 60% and 70% solution: none was found within the reported error limits.

(c) Uptake experiment on a fast droplet train (200 μm diameter 73% H_2SO_4-H_2O droplets) traversing a flow tube coupled to a multiple pass IR diode laser absorption cell of 728 cm optical path at pressures of 10 Torr and droplet-gas interaction times of 1–2 ms. The product branching ratio for the heterogeneous N_2O_5-H_2O interaction was defined as the ratio of observable $HNO_3(g)$ and twice the depletion of $N_2O_5(g)$ $[(HNO_3(g))/2\Delta(N_2O_5(g))]$, and varied between 0.25 and 0.37 for interaction times of 1.1 to 1.6 ms, respectively. The value for γ listed in the Table has been corrected for gas-phase diffusion and distortion of the Maxwellian velocity distribution near an adsorbing surface and is about 40% larger than in pure water. No saturation effects have been observed due to the high reactivity of the heterogeneous interaction.

(d) Knudsen cell technique using electron-impact MS detection using modulated molecular beam phase-sensitive detection. N_2O_5 was detected at m/e 46 and HNO_3 detected at m/e 30, 46, and 63 (for high densities). The concentration of HNO_3 was in the range 4×10^{10} to 10^{12} molecule cm^{-3}. The uptake on 74 to 96% H_2SO_4 did not saturate around temperatures of 220 K for the duration of the experiment (1000 s) if the raw signal for N_2O_5 uptake was corrected for the formation of HNO_3 which increased slowly with time. The uptake experiments resulted in a temperature concentration (74 to 96% H_2SO_4) and time-independent γ value of 0.02–0.03. Saturation effects were thought to affect the measurement of γ even at low densities (2×10^{11} molecule cm^{-3}). Stirring the H_2SO_4-H_2O solution increased γ by a factor of 2 to 3, resulting in a value displayed in the Table. At γ=0.1 it takes a few seconds to saturate the sulfuric acid surface at the lowest densities used.

(e) Uptake experiment in high-pressure (0.3–0.8 atm) flow tube using slow flow conditions and fine size-selected (classified) aerosol. The sulfuric acid aerosol size ranged from 60 to 250 nm diameter at 225 to 293 K, corresponding to a sulfuric acid content of 54% to 82%, and was generated by homogeneous nucleation from the reaction of SO_3 + H_2O. The N_2O_5 concentration ranged from 30 to 200 ppb at 333 to 800 mbar total pressure. The N_2O_5 detection was performed by observing the decrease in NO concentration after reaction in a heated quartz tube using tunable diode laser absorption which was also used to monitor the partial pressure of H_2O vapor. Corrections to the decay curves of N_2O_5 as a function of reaction time amounted to less than 20% each and were principally due (i) to the presence of doubly charged aerosol particles in the aerosol classifier, (ii) to deviation from plug flow conditions and (iii) to gas-phase diffusion towards the aerosol surface. For each temperature and rh, N_2O_5 decays were obtained for several particle sizes and number densities of aerosol particles. No dependence of the N_2O_5 uptake coefficient on particle size was detected within the experimental conditions. At 293 and 273 K, γ_{ss} (see Table) was independent of the H_2SO_4 composition but seemed to depend on composition at lower temperatures. At 260 K, γ_{ss} is independent of composition for sulfuric acid concentrations up to, but excluding, 78% H_2SO_4. At this composition and temperature there was an indication that $\gamma_{ss}=4\times10^{-2}$ for a frozen aerosol and $\gamma_{ss}=1.8\times10^{-1}$ for the aerosol in the supercooled state. At 230 K, γ_{ss} increased from 7.7×10^{-2} for compositions near 60% H_2SO_4 to 1.46×10^{-1} for compositions near 70% H_2SO_4. Intermediate conditions resulted in intermediate results. A semiempirical model was put forward that explains the trends of γ_{ss} as a function of temperature and composition (rh). There were indications from this work that the sulfuric acid aerosol is in a supercooled state at $T\leqslant260$ K.

(f) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of N_2O_5 in the presence of HNO_3 and other reactants at characteristic densities of 10^9 to 10^{11} molecule cm^{-3}. The cryogenic deposits were characterized by their vapor pressure of H_2O, detected by an ion-molecule reaction with F_2^-, whose decrease with the H_2O vapor pressure was monitored. The sulfuric acid surfaces were prepared by freezing a small amount of 57.7% H_2SO_4 (tetrahydrate) or 60% H_2SO_4 on the inside of the flow tube wall. The results were obtained as a function of rh, which was varied by adjusting the temperature of the frozen phase at a constant H_2O flow rate of 0.25 mTorr or by changing the H_2O flow rate at constant temperature to result in a range 10%–90% rh. The uptake coefficients were determined from the decrease of the N_2O_5 density ($\sim10^{-7}$ Torr) with residence time. For 57.5% H_2SO_4 (tetrahydrate) they were almost independent of rh and were much lower than those found for liquid acid. The uptake coefficient determined for 60% H_2SO_4 at 192 K depended on rh (a decrease of a factor of 4 in going from 80% to 40% rh) whereas the one measured at 205 K was independent on rh within experimental error.

(g) For experimental details, see Comment (l). A bulk solution of HNO_3-H_2O corresponding to NAT stoichiometry was frozen to 188 K. The initial value for γ drops from the maximum given in the Table to a value of less than 0.01, typically 0.004 which is the steady-state asymptote for NAT. Uptake was studied on other cryogenic surfaces containing HNO_3-H_2O in variable amounts. No consistent picture emerges as γ always goes through a maximum. There is concern that the bulk cryogenic phase did not correspond to NAT in those studies owing to the high reactant pressures used but was in fact a supercooled liquid glass.

(h) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of N_2O_5 in the presence of HNO and other reactants at characteristic densities of 10^9 to 10^{11} molecule cm^{-3}. NAT was prepared *in situ* by converting N_2O_5 into HNO_3 on the ice surface well past saturation. The steady-state HNO_3 vapor detected at the downstream end of the flow tube was consistent, within a factor of two, with the expected equilibrium vapor pressure over NAT-HNO_3-in-ice solid solution near 201 K. From the N_2O_5 taken up by the cryogenic substrate, a NAT layer 1 to 2 monolayers thick [(2–4) $\times10^{14}$ HNO_3 cm^{-2}] was inferred. It was assumed that the saturated monolayer was at steady-state for the duration of the experiment. Saturation effects on pure ice were observed at N_2O_5 concentrations varying from 10^9 to 3×10^{10} molecule cm^{-3}. No saturation effects of γ on NAT have been reported. The relevant surface corresponds to the geometric area, as an increase of the ice mass by a factor of 5 to 10 had no noticeable effect on γ.

(i) For experimental details see Comment (h). These experiments were designed to investigate the influence of the thickness of the substrate on γ. The values for γ given in the Table correspond to a thickness of 10 μm where one can expect a coherent film of substrate deposited from the vapor phase (see Kenner *et al.*[13]). The value for γ varied by a factor of no more than three and 1.5 for NAT and pure ice, respectively, when the thickness was varied from 1 to 100 mm. The conclusion is that there is no significant dependence of γ on thickness.

(j) For experimental details see Comments (h) and (i). This study was undertaken to supplement the original work on ice and nitric-acid doped (NAT) surfaces to further confirm the independence of the measured uptake coefficients on the substrate thickness.

(k) Uptake experiment in an ice-coated flow tube with MS detection in the ioncounting mode at m/e 30, 46, and 63. Characteristic N_2O_5 density of $(1–10)\times10^{10}$ molecule cm^{-3} was used. Owing to the large difference between γ for ice and NAT, poisoning effects led to hysteresis behavior in the experimental data of N_2O_5 density vs. injector position as the injector was moved back and forth. The reaction product HNO_3 forms NAT in the course of the experiment. The results listed in the Table correspond to the initial value of γ. The geometric surface is the relevant area for the uptake experiment. Numerical modeling was used to interpret the experimental results. The simple model based on $N_2O_5(g) + sf\ H_2O(s) \rightarrow 2(HNO_3\cdot3H_2O)(s)$ satisfactorily explained the major features of the data resulting in a modeled γ of 0.015 and sf=7±3 in accord with the hypothesis that initial reaction occurs on ice sites. A small negative temperature dependence for γ (5–10 kJ mol^{-1}) was noted. The poisoning effect consists in blocking free available water sites on which the reaction takes place by converting them into NAT. The model results were independent of the thickness of the ice (d) for d>9 μm which seems to be the minimum thickness which still gave a coherent ice coat on the wall of the flow tube.

(l) Uptake experiment in a low pressure Knudsen cell flow reactor monitored by modulated molecular beam electron-impact MS. The ice was condensed from the vapor phase, and the uptake experiment was performed at typical pressures of N_2O_5 of 1.0 mTorr. The uptake coefficient γ was monitored using the MS signal at m/e 46, where HNO_3 also contributed significantly; due to the high pressure of N_2O_5 used the vapor pressure of bulk HNO_3 (multilayers) significantly perturbed the quantitative measurement of γ so that only a lower limit could be given. The reaction was also followed by observing the identity of the reaction product (HNO_3) through its thermal desorption behavior when the cryogenic phase was allowed to warm up after the reaction. HNO_3 monitored at m/e 63 desorbed both at 203 (bulk or "overlayer") and around 230 K (unspecified hydrate). The corresponding H_2O signal recorded at m/e 18 showed two characteristic desorption temperatures, 209 K and 230 K; the former corresponds to free (bulk) H_2O whereas the latter corresponds to the dissociation of the HNO_3 hydrate (a temperature also found from reference experiments by co-condensing HNO_3 and H_2O). The yield of HNO_3 with respect to N_2O_5 was 1.3 (the expected value is 2.0 if the only reaction product is HNO_3 and if all HNO_3 formed desorbed into the gas phase).

(m) Ice-coated flow tube coupled to electron-impact MS. The ice film was deposited from water vapor and the typical N_2O_5 concentration was 1×10^{13} molecule cm^{-3}. The kinetics were measured by monitoring the disappearance of N_2O_5 at m/e 46 under conditions where HNO_3 remained on the ice film. Corrections of γ due to diffusion limitations were performed using estimated diffusion coefficients scaled to 195 K. A fresh ice film was prepared for every uptake experiment.

(n) Uptake experiment in a low pressure Knudsen cell flow reactor monitored by modulated molecular beam electron-impact MS. Pure ice from freezing liquid water (bulk) and condensed from the vapor phase (film, 5000 monolayers). No HNO_3 was observed. Monitored N_2O_5 using m/e 46. Characteristic pressure was on the order of 10^{11} molecule cm^{-3}. Unusual behavior of γ with time of exposure was observed: Uptake started at 0.01, then increased with time (maximum values given in Table) and subsequently tended towards a steady state at 0.004 (characteristic of NAT at long exposure times). This behavior was interpreted qualitatively as a combination of autocatalytic and saturation behavior. The number of N_2O_5 taken up to maximum γ was constant for all the experiments performed (4.6×10^{16} molecule or twice that in HNO_3). The geometric surface of ice seems to be the relevant area for uptake. Bulk and film values for γ are identical within the experimental uncertainty.

(o) Uptake experiment on a fast droplet train (200 μm diameter) crossing a flow tube in transverse geometry. Trace gas analysis was by IR diode laser absorption in a multiple pass cell of 728 cm optical path at total pressures of 5–20 Torr. Values listed are corrected for gas-phase diffusion and distortion of velocity vector owing to rapid uptake.

(p) Uptake experiment involving the interaction of N_2O_5 in an atmospheric pressure of synthetic air with a liquid jet of pure water. The uptake kinetics was studied by analyzing the liquid water content for NO_3^- or Cl^- using ion chromatography. The jet diameter was 90 μm and the jet length between 0.2 and 6 mm leading to contact times of 0.03–1.0 ms. The uptake coefficient was interpreted as a mass accommodation coefficient after fitting of the concentration of anions in the collected sample with the jet length taking into account the diffusion coefficients for the gas and liquid phase as well as the Henry's law constants. The results are regarded as lower limits owing to uncertainties in the velocity distribution of the liquid jet. The N_2O_5 concentration detected by UV absorption in the 200 to 224 nm range was about 100 ppm and the 10% HNO_3 impurity was taken into account in the fitting procedure. Less than 2 ppm of NO_2 was detected using LIF excited at 442 nm and a measurement of γ relative to the one for HCl ($\gamma=1.0\times10^{-2}$) resulted in a γ value larger by a factor of two with respect to the absolute determination.

(q) Uptake experiment on a fast droplet train (80–150 μm diameter) inside a flow tube at total pressures of 20–60 Torr synthetic air with 4–16 ms contact time. The temperature of the droplet was controlled by the metered partial pressure of H_2O in the synthetic air carrier gas which was varied between 1.9 to 6.2 Torr (262–277 K). The N_2O_5 contained less than 8% HNO_3 and its partial pressure monitored by FTIR absorption ranged from 20 to 2000 ppm in the flow tube. The extent of reaction was followed by measuring the NO_3^- concentration in the collected droplets using HPLC. It was found that negligible loss of N_2O_5 occurred when the relative humidity was kept below 30% in the Teflon FEP tubing. The uptake coefficients were corrected for gaseous diffusion of N_2O_5 to the droplet surface. It is thought that the uptake coefficient is reaction controlled with a pseudo-first-order rate constant of $\sim10^5$ s^{-1}.

(r) Uptake experiment in a low pressure Knudsen cell monitored by electron-impact MS. The substrate was commercially available charcoal material with a BET surface area of 37 $m^2 g^{-1}$. The first entry in the table refers to uptake of N_2O_5 on charcoal in the absence of added H_2O at a characteristic N_2O_5 concentration of 15.1×10^{14} molecule cm^{-3}. Main reaction product was NO from redox reaction on charcoal, HNO_3 was observed at m/e 63 as a minor product. The second entry refers to N_2O_5 uptake in the presence of H_2O after steady state regarding N_2O_5 adsorption had been attained. Physisorption, redox reaction, and hydrolysis are all taking place with the added complication of secondary heterogeneous reaction of the hydrolysis product HNO_3 on the carbon surface. Therefore, the value for γ in the second entry has to be regarded as a lower limit for the uptake coefficient of N_2O_5. In the initial stages of the uptake the redox reaction dominates, and after saturation of the reaction sites HNO_3 starts desorbing after about 20 min. Mass balance data indicate that 30% of the N_2O_5 undergoes redox reaction and/or physisorption at steady state at H_2O concentrations that maintain constant water coverage on the substrate. With increasing H_2O concentration an increased rate of HNO_3 formation is observed. In the later stages of the interaction the hydrolysis gains in importance in relation to the redox chemistry. This is apparent in an increase of both the rate of H_2O consumption and HNO_3 formation at the expense of the rate of NO formation. At steady state the rate law for HNO_3 formation is linear in $[HNO_3]$ and $[H_2O]$ under excess conditions of the other reaction partner.

Preferred Values

The uptake coefficient of N_2O_5 on *liquid* sulfuric acid substrates at temperatures around 220 K seems to fall between 5×10^{-2} to 1×10^{-1} for surfaces of bulk substrates. The results obtained on fine sulfuric acid *aerosols* at comparable temperatures seem to lie on the upper bound of the range and may have gone through a maximum around 250 K ($\gamma_{max} = 0.15$). The uptake coefficient on *frozen* bulk sulfuric acid at slightly lower temperatures (200 K) is 5×10^{-3} which is roughly an order of magnitude lower than the one for the bulk liquid. Although most of the measurements suggest that this reaction is largely independent of the sulfuric acid content (water activity) and fairly insensitive to temperature changes, both of which cannot easily be varied independently in most experiments, the most recent experiments of Fried *et al.*[7] reveal dependencies on both temperature and composition.

On NAT-like substrates the uptake coefficient attains a value on the order of 5×10^{-4} which is the result of several determinations using the same technique (flowing gas). The experiments seem to be prone to saturation effects.

The uptake on a water ice film at 190 K results in $\gamma=2\times10^{-2}$, both for ice films deposited from the vapor phase as well as for bulk ice. This value is smaller than the one for uptake on liquid H_2SO_4-H_2O at comparable temperatures, by a factor of three. A γ value of 4×10^{-2} is obtained for the uptake on supercooled and liquid water droplets at subambient temperatures (260 to 280 K).

References

[1] M. Mozurkewich and J. G. Calvert, J. Geophys. Res. **93**, 15889 (1988).

[2] D. R. Hanson and A. R. Ravishankara, J. Geophys. Res. **96**, 17307 (1991).

[3] J. M. Van Doren, L. R. Watson, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. **95**, 1684 (1991).

[4] D. M. Golden, J. A. Manion, C. M. Reihs, and M. A. Tolbert, in *CHEMRAWN VII: Chemistry of the Atmosphere: The Impact of Global Change*, edited by J. G. Calvert (Oxford University Press, New York, 1992).

[5] L. R. Williams, J. A. Manion, D. M. Golden, and M. A. Tolbert, J. Appl. Meteorol. **33**, 785 (1994).

[6] J. A. Manion, C. M. Fittschen, D. M. Golden, L. R. Williams, and M. A. Tolbert, Isr. J. Chem. **34**, 355 (1994).

[7] A. Fried, B. E. Henry, J. G. Calvert, and M. Mozurkewich, J. Geophys. Res. **99**, 3517 (1994).

[8] D. R. Hanson and A. R. Ravishankara, J. Geophys. Res. **98**, 22931 (1993).

[9] M. A. Quinlan, C. M. Reihs, D. M. Golden, and M. A. Tolbert, J. Phys. Chem. **94**, 3255 (1990).

[10] D. R. Hanson and A. R. Ravishankara, J. Geophys. Res. **96**, 5081 (1991).

[11] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **96**, 2682 (1992).

[12] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **97**, 2802 (1993).

[13] R. D. Kenner, K. R. Ryan, and I. C. Plumb, J. Phys. Chem. (1994).

[14] M. A. Tolbert, M. J. Rossi, and D. M. Golden, Science **240**, 1018 (1988).

[15] M.-T. Leu, Geophys. Res. Lett. **15**, 851 (1988).

[16] J. M. Van Doren, L. R. Watson, P. Davidovits, D. R. Worsnop, M. Zahniser, and C. E. Kolb, J. Phys. Chem. **94**, 3265 (1990).

[17] W. Kirchner, F. Welter, A. Bongartz, J. Kames, S. Schweighoefer, and U. Schurath, J. Atm. Chem. **10**, 427 (1990).

[18] C. George, J. L. Ponche, P. Mirabel, W. Behnke, V. Scheer, and C. Zetzsch, J. Phys. Chem. **98**, 8780 (1994).

[19] L. Brouwer, M. J. Rossi, and D. M. Golden, J. Phys. Chem. **90**, 4599 (1986).

$N_2O_5 + HCl \rightarrow HNO_3 + NO_2Cl$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\geq 3\times10^{-3}$	ice film, 15–32% HCl	185	Tolbert, Rossi, and Golden, 1988[1]	(a)
γ_{ss}	$(2.7\pm1.0)\times10^{-2}$	ice film, $p_{HCl} \rightarrow 0.0$	195	Leu, 1988[2]	(b)
γ_{ss}	$(3.2\pm1.0)\times10^{-3}$	NAT film	200	Hanson and Ravishankara, 1991[3]	(c)

Comments

(a) Uptake experiment in a low pressure Knudsen cell flow reactor monitored by modulated molecular beam electron-impact MS. The ice phase was condensed from H_2O vapor prior to the uptake experiment, and a HCl-H_2O ice (7 and 14% on a per mole basis) was prepared by co-condensation of both components. The characteristic N_2O_5 pressure was 12 mTorr. The uptake coefficient was measured at m/e 46 assuming only N_2O_5 and $ClNO_2$ in the Knudsen cell effluent. Therefore, γ given in the Table is a lower limit. Nitryl chloride, NO_2Cl, was confirmed as a gas-phase product together with condensed HNO_3, which was identified by thermal desorption experiments performed after the uptake experiment. No interaction of NO_2Cl with the solid solution of HCl-H_2O at 185 K was observed. An added complication in those experiments was the fast heterogeneous reaction of N_2O_5 with HCl on the cold reactor walls in the absence of a cryogenic H_2O film, resulting in identical reaction products. All but 5% of the originally co-condensed HCl was converted into $ClNO_2$.

(b) Uptake experiment in an ice-coated flow tube coupled to electron-impact MS. The HCl-ice film was deposited from simultaneous condensation of H_2O and HCl vapor and the typical N_2O_5 concentration was 1×10^{13} molecule cm^{-3}. The composition of the HCl-ice film was determined after each experiment: the HCl mole fraction ranged from 0.015–0.04. A fresh ice film was prepared for every uptake experiment. The kinetics were measured by monitoring the disappearance of N_2O_5 at m/e 46 under conditions where HNO_3 remained on the ice film. $ClNO_2$ or ClONO was observed at m/e 49/51, and uptake coefficients measured using m/e 46 signals were corrected for the contribution of those two (volatile) products. Corrections of γ for diffusion limitations were performed using estimated diffusion coefficients scaled to 195 K. The value of γ listed corresponds to a limiting value for the mole fraction of HCl in the ice (f_{HCl}) approaching zero: $\gamma=0.051$ at $f_{HCl}=0.015$, $\gamma=0.063$ at $f_{HCl}=0.04$.

(c) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of N_2O_5 in the presence of HNO_3 and other reactants at characteristic densities of 10^9-10^{11} molecule cm^{-3}. NAT was prepared *in situ* by converting N_2O_5 into HNO_3 well past saturation of the ice surface. The steady state HNO_3 vapor detected at the downstream end of the flow tube was consistent within a factor of two with the equilibrium vapor pressure over NAT-HNO_3-in-ice solid solution near 201 K. From the N_2O_5 taken up by the cryogenic substrate a NAT layer 1 to 2 monolayers thick [$(2–4)\times10^{14}$ HNO_3 molecule cm^{-2}] was inferred. It is assumed that the saturated monolayer is at steady-state over the duration of the experiment. The experiments were performed under conditions of a steady state concentration of HCl twice that of N_2O_5, namely between (2–6) $\times10^9$ molecule cm^{-3}, because the reaction was controlled by the availability of HCl. When the reaction was performed on pure ice no effect of the added HCl could be detected, thus indicating no preference for reaction of N_2O_5 with HCl over that with H_2O. Since the uptake on ice is faster by a factor of eight, the reactive uptake of N_2O_5 in the presence of HCl was studied on a NAT surface. No information regarding the saturation of γ on the NAT surface is available. The relevant surface corresponds to the geometric area as an increase of the ice mass by a factor of 5 to 10 had no noticeable effect on γ.

References

[1] M. A. Tolbert, M. J. Rossi, and D. M. Golden, Science **240**, 1018 (1988).
[2] M.-T. Leu, Geophys. Res. Lett. **15**, 851 (1988).
[3] D. R. Hanson and A. R. Ravishankara, J. Geophys. Res. **96**, 5081 (1991).

$N_2O_5 + HBr \rightarrow BrONO + HNO_3$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\sim5\times10^{-3}$	H_2O-ice, NAT	201	Hanson and Ravishankara, 1992[1]	(a)

Comments

(a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS with selective detection of HBr and other halogen containing reactants and products. Ice layers 2–10 μm thick were condensed from the vapor phase onto the cold flow tube wall and HNO_3-treated ice was defined as NAT under the given experimental conditions. On cold Pyrex, γ_{ss} was found to be $<10^{-4}$ whereas γ_{ss} based on the disappearance of N_2O_5 increased to $\sim5\times10^{-3}$ at 50% rh at HBr concentrations of 5×10^9 to 10^{11} molecule cm^{-3}. Without HBr the N_2O_5 loss is much smaller ($\gamma_{ss}\sim1\times10^{-3}$, consistent with the small uptake coefficient for N_2O_5 on NAT) such that the difference to 5.0×10^{-3} is attributed to the reaction probability of the title reaction. At higher N_2O_5 and HBr concentrations a new distinct phase forms that is visible to the eye with γ_{ss} $\sim4\times10^{-2}$ with no intermediate values observed. On pure H_2O-ice and NAT the same results were obtained as on cold Pyrex at 50% rh. An alternative reaction path leading to $BrONO_2$ + HONO could not be excluded. It has to be noted that BrONO was not observed in these experiments as it is an inferred reaction product.

References

[1] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **96**, 9441 (1992).

$N_2O_5 + NaCl \rightarrow ClNO_2 + NaNO_3$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$\geq 2.5\times 10^{-3}$		300	Livingston and Finlayson-Pitts, 1991[1]	(a)
γ_{ss}	$(3.2\pm 0.3)\times 10^{-2}$	high rh	292	Zetzsch and Behnke, 1992[2]	(b)
				Behnke *et al.*, 1992[2], 1994[4,5]	
γ_{ss}	$(3.9\pm 1.3)\times 10^{-2}$	H_2O droplet	263	George *et al.*, 1994[6]	(c)
	$(1.4\pm 0.8)\times 10^{-2}$	H_2O droplet	278		

Comments

(a) The N_2O_5 exposure experiments were conducted in a static salt-packed cylindrical cell whose content was monitored by long path FTIR absorption spectroscopy at 1 atm pressure. HNO_3, N_2O_5, and NO_2Cl were observed in the spectral range 700–1500 cm^{-1} and the uptake coefficient was inferred from the fractional yield of NO_2Cl relative to N_2O_5 as a function of residence time and mass of the salt. The typical initial concentration of N_2O_5 in the vessel containing the salt was approximately 5.5×10^{13} molecule cm^{-3}. The salt had a surface area of 33 cm^2 g^{-1} and small amounts of water vapor did not affect the results. Large amounts of HNO_3 ($HNO_3/N_2O_5=0.55\pm 0.16$) originating from the heterogeneous reaction of N_2O_5 with residual water resulted in the formation of HCl.

(b) The N_2O_5 uptake experiments were performed in an aerosol smog chamber with Teflon coated walls in a mixture of hydrocarbons, NO_x, and O_3 and in the presence of a well characterized NaCl aerosol with known size distribution. Typical conditions were 60 ppb of N_2O_5 in air, 80 mg m^{-3} of NaCl and relative humidities of 71–92% (292 K). The extent of the reaction was followed by monitoring the decrease of the hydrocarbons, O_3, HCl, and NO_2 as a function of time. The amount of N_2O_5 taken up was assessed using the NO_x mass balance and $ClNO_2$ was derived from the hydrocarbon consumption with time in the presence of light (arising from the reaction Cl + hydrocarbon). The uptake coefficient γ based on the disappearance of N_2O_5 was independent of relative humidity for the range given above, whereas the yield of $ClNO_2$ varied strongly with relative humidity. The results on $ClNO_2$ were discussed in terms of a branching ratio k_a/k_b between $N_2O_5(ads) + NaCl \rightarrow NaNO_3 + ClNO_2$ (k_a) and $N_2O_5(ads) + H_2O \rightarrow 2HNO_3$ (k_b). The yields were 100%, 75%, 50%, and 33% $ClNO_2$ for rh of 50%, 71%, 76% (deliquescence point of NaCl), and 92% based on N_2O_5 taken up. Recent results point towards a constant $ClNO_2$ yield of 70%, corresponding to a branching ratio of 2.5:1 independent of the relative humidities between 50 and 92% (corresponding to [NaCl] of 6 to 2.2 M). The yields were corrected for the formation of alkyl nitrates that were calculated from a standard photochemical model. The chlorinated hydrocarbons 1,1-dichloroacetone, chloroacetone, and phosgene probably resulted from the heterogeneous interaction of Cl with the hydrocarbons and were detected by GC. The $ClNO_2$ yields observed from experiments in a wetted-wall flow tube decreased continuously for [NaCl]≤2 M corresponding to 94% rh but were still at 20% at $[NaCl]=1.7\times 10^{-2}$ M. The results from the smog chamber and wetted-wall flow tube experiments agree well in the overlapping range.

(c) Uptake experiment on a fast droplet train (80–150 μm diameter) inside a flow tube at total pressures of 20–60 Torr synthetic air with 4–16 ms contact time containing 1 M NaCl. The temperature of the droplet was controlled by the metered partial pressure of H_2O in the synthetic air carrier gas which was varied between 2.1–6.2 Torr (263–278 K). The N_2O_5 contained less than 8 HNO_3 and its partial pressure monitored by FTIR absorption ranged from 20 to 2000 ppm in the flow tube. The extent of reaction was followed by measuring the NO_3^- concentration in the collected droplets using HPLC. It was found that negligible loss of N_2O_5 occurred when the rh was kept below 30% in the Teflon FEP tubing. The measured uptake coefficients were corrected for gaseous diffusion of N_2O_5 to the droplet surface and the NO_2Cl yield (67±7%) obtained from independent wetted-wall flow tube experiments. The reactive uptake coefficients on droplets containing NaCl are slightly larger than those for droplets without NaCl. It is thought that the uptake coefficient is reaction controlled rather than given by mass accommodation.

References

[1] F. E. Livingston and B. J. Finlayson-Pitts, Geophys. Res. Lett. **18**, 17 (1991).

[2] C. Zetzsch and W. Behnke, Ber. Bunsenges. Phys. Chem. **96**, 488 (1992)

[3] W. Behnke, H.-U. Kruger, V. Scheer, and C. Zetzsch, J. Aerosol Sci. **S23**, S933 (1992)

[4] W. Behnke, H.-U. Kruger, V. Scheer, and C. Zetzsch, Physico-Chemical Behavior of Atmospheric pollutants, **1994**, pg. 960 (EUR 15609)

[5] W. Behnke, C. H. George, V. Scheer, and C. Zetzsch, The Proceedings of EUROTRAC Symposium '94 edited by P. M. Borrell *et al.*, **1994** (SPB Academic Publishing bv, The Hague, The Netherlands), p. 1064.

[6] C. George, J. L. Ponche, P. Mirabel, W. Behnke, V. Scheer, and C. Zetzsch, J. Phys. Chem. **98**, 8780 (1994).

$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$

(including uptake studies)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
	Sulfate/H_2SO_4 (liquid) Substrates				
γ_{ss}	$(3.2\pm0.8)\times10^{-4}$	95.6% H_2SO^4	300	Rossi, Malhotra, and Golden, 1987[1]	(a)
γ_{ss}	2.6×10^{-3}	65% H_2SO_4	210	Tolbert, Rossi, and Golden, 1988[2]	(b)
	3.0×10^{-4}	75% H_2SO_4	230		
γ_{ss}	$(6.4\pm1.0)\times10^{-2}$	40% H_2SO_4	218±3	Hanson and Ravishankara, 1991[3]	(c)
	$(3.1\pm0.5)\times10^{-3}$	60% H_2SO_4	215		
	$(1.2\pm0.2)\times10^{-3}$	65% H_2SO_4	215		
	$(3.9\pm0.7)\times10^{-4}$	70% H_2SO_4	220		
	$(1.9\pm0.3)\times10^{-4}$	75% H_2SO_4	230		
γ_{ss}	$(8.1\pm1.3)\times10^{-2}$	40% H_2SO_4	220±5	Golden *et al.*, 1992[4]; Williams *et al.*, 1994[5]; Manion *et al.*, 1994[6]	(d)
	$(4.1\pm0.7)\times10^{-3}$	57.5% H_2SO_4	220±5		
	$(2.1\pm0.35)\times10^{-4}$	75% H_2SO_4	220±5		
γ_{ss}	$(3.8\pm1.2)\times10^{-2}$	46.6% H_2SO_4, liquid	202	Hanson and Ravishankara, 1994[7]	(e)
	$(6.1\pm2.0)\times10^{-3}$	57.5% H_2SO_4, liquid	202		
	$(9.3\pm3.0)\times10^{-4}$	65% H_2SO_4, liquid	202		
	Sulfate/H_2SO_4 (solid) Substrates				
γ_{ss}	2.0×10^{-3}	57.7% H_2SO_4, 90% rh	191.5	Hanson and Ravishankara, 1993[8]	(f)
	2.0×10^{-3}	57.7% H_2SO_4, 30% rh	196		
	5.0×10^{-4}	57.7% H_2SO_4, 16% rh	200		
	1.0×10^{-4}	57.7% H_2SO_4, 7% rh	205		
γ_{ss}	$(1.6\pm0.4)\times10^{-2}$	SAT, H_2O-rich, 100% rh	195	Zhang, Jayne and Molina, 1994[9]	(g)
	$(5.0\pm1.3)\times10^{-4}$	SAT, H_2SO_4-rich, 0.8% rh	195		
	HNO_3-H_2O Substrates				
γ_{ss}	$(6.0\pm2.0)\times10^{-3}$	NAT film	201	Hanson and Ravishankara, 1991[10]	(h)
γ_{ss}	1.0×10^{-5}	NAT film	196	Leu, Moore, and Keyser, 1991[11]	(i)
γ_{ss}	$(2.0\pm0.8)\times10^{-3}$	NAT film	191	Hanson and Ravishankara, 1992[12]	(j)
	$(4.0\pm1.6)\times10^{-3}$	NAT film	201		
	$(8.0\pm3.2)\times10^{-3}$	NAT film	211		
γ_{ss}	$(2.0\pm1.0)\times10^{-3}$	NAT film, H_2O-rich	202	Abbatt and Molina, 1992[13]	(k)
	$(5.0\pm2.5)\times10^{-3}$	NAT film, HNO_3-rich	202		
γ_{ss}	$(1.0\pm0.3)\times10^{-3}$	NAT film	191	Hanson and Ravishankara, 1993[14]	(l)
γ_{ss}	2.0×10^{-3}	NAT, 90% rh	191	Hanson and Ravishankara, 1993[8]	(f)
	5.0×10^{-4}	NAT, 50% rh	194		
	3.0×10^{-4}	NAT, 25% rh	198		
γ_{ss}	$(2.0\pm0.3)\times10^{-3}$	NAT, H_2O-rich, 100% rh	195	Zhang, Jayne, and Molina, 1994[9]	
	H_2O (solid) Substrates				
γ_{ss}	$(9.0\pm2.0)\times10^{-3}$	ice film	185	Tolbert *et al.*, 1987[15]	(m)
γ_{ss}	$(6.0\pm3.0)\times10^{-2}$	ice film	200	Leu, 1988[16]	(n)
γ_{ss}	$0.3^{+0.7}_{-0.1}$	ice film	201	Hanson and Ravishankara, 1991[3]	(h)
γ_{ss}	$(5.0^{+5.0}_{-4.0})\times10^{-3}$	ice film	196	Leu, Moore, and Keyser, 1991[11]	(i)
γ_{ss}	$0.8^{+0.2}_{-0.3}$	ice film	191	Hanson and Ravishankara, 1992[12]	(j)
γ_{ss}	0.30 ± 0.10	ice film	191	Hanson and Ravishankara, 1993[14]	(l)
γ_{ss}	3.0×10^{-2}	thin ice film	188	Chu, Leu, and Keyser, 1993[17]	(o)
	1.3×10^{-1}	thick ice film	188		
γ_{ss}	$(8.0\pm2.0)\times10^{-2}$	ice film	195	Zhang, Jayne, and Molina, 1994[9]	(g)

Comments

(a) Uptake experiment in a two-chamber Knudsen cell using molecular beam modulated electron-impact MS. Simultaneous flows of H_2O (1.5×10^{13} molecule cm^{-3}) and $ClONO_2$ (9.4×10^{11}–4.5×10^{13} molecule cm^{-3}) were exposed to bulk 95.6% H_2SO_4 at ambient temperature. The uptake kinetics were monitored at m/e 46 ($ClONO_2$) and HOCl was measured at m/e 51/53 as the sole product released into the gas phase. The uptake coefficient was independent of the density of $ClONO_2$ and thus first order. The γ value listed in the Table corresponds to a steady-state value and was approximately a factor of three higher in the beginning of the experiment. In the absence of a continuous H_2O flow the HOCl signal decreased only by 25%, and the formation of Cl_2O was detected under conditions of prolonged exposure of $ClONO_2$ to H_2SO_4 and thus prolonged generation of HOCl. No measurable uptake ($\gamma \leqslant 10^{-5}$) was reported for $ClONO_2$ uptake on 95.6% H_2SO_4 at 185 K (Tolbert *et al.*[15]).

(b) Uptake experiment in a Knudsen cell flow reactor coupled to a modulated molecular beam sampled electron-impact MS. The bulk substrate (1–5 mL) was cooled slowly to temperatures of 210–230 K. The H_2SO_4 concentration in the bulk was obtained by dilution from 96.5% H_2SO_4 and was chosen to reflect the sulfuric acid aerosol concentration under stratospheric conditions, that is, in the temperature range 210–230 K and a vapor pressure of 4×10^{-4} Torr ($\pm30\%$) which was the measured steady-state vapor pressure in the Knudsen cell. The measured values were measured under steady-state conditions with $ClONO_2$ monitored at m/e 46. The corresponding rate coefficient for uptake of $ClONO_2$ followed a first-order rate law and both HOCl and some Cl_2O reaction products were observed. The desorption behavior of HNO_3 incorporated into bulk 75% H_2SO_4 as a result of uptake of $ClONO_2$ at 230 K was very similar to that from HNO_3 interaction on the same substrate: apparent peak of HNO_3 desorption (almost certainly an artifact) was at 251 K and approximately 20% recovery.

(c) Uptake experiment in a wetted-wall flow tube with chemical ionization MS detection. This method allows selective detection of $ClONO_2$ in the presence of HNO_3 and other reactants at characteristic densities of 10^{10} to 10^{11} molecule cm^{-3}, for product studies it was of the order of 10^{12} molecule cm^{-3}. The cold aqueous solution of H_2SO_4 (40 to 75% by weight, T=215 to 230 K) was flowing down the walls of the flow tube with a liquid film residence time of 20–30 s. $p(H_2O)$ was generally around 1 mTorr. The $ClONO_2$ reaction seems to be a reactive process as HOCl was observed over the 40% and 60% H_2SO_4 solutions (large value of γ). For the 60% H_2SO_4 solution at 263 K the yield of HOCl was estimated to be about one half of the consumed $ClONO_2$, with the remainder presumably dissolved in the solution. Temperature-dependent uptake experiments of $ClONO_2$ over 60%, 65%, 70%, and 75% solutions up to 260 K resulted in essentially no temperature dependence of γ outside the reported error limits.

(d) Knudsen cell flow reactor technique with electron-impact MS detection using modulated molecular beam phase sensitive detection. $ClONO_2$ detected at m/e 46 and HOCl detected at m/e 51/53. p_{ClONO_2} was in the range 10^{12} to 10^{13} molecule cm^{-3}. The uptake on 40–75% H_2SO_4 did not saturate around temperatures of 220 K for the duration of the experiment (1000 s), and HOCl formation was delayed and increased on the same time scale. The following analytical expression for the uptake/reaction probability (γ) of $ClONO_2$ at 220 K was obtained: $\log \gamma=\{1.87-0.074\ (\%H_2SO_4)\}$ ($\pm15\%$) which is valid for the range of 40% to 80% H_2SO_4/H_2O mixtures.

(e) Uptake experiment in a laminar-flow tube of gas-phase $ClONO_2$ onto a quiescent liquid surface with chemical ionization detection MS as a partial pressure monitor. H_2SO_4 (46.6% to 65%) was applied as a cold liquid to the inner wall of the flow tube. The liquid H_2SO_4 with a residual HCl content of less than 10^{-4} mol dm^{-3} was back-titrated after the uptake experiment, and the product HOCl was only qualitatively detected. The first order loss rate coefficients were based on the disappearance of $ClONO_2$ and were $\geqslant 10\ s^{-1}$. No significant temperature dependence of the uptake coefficient in the temperature range 200–220 K was observed. A simultaneous fit using two adjustable parameters resulted in fitted values for γ_{ss} that were less than 10% of the measured values. The second order rate coefficient k_{HCl}^{II} for the title reaction in the bulk liquid has been estimated to be $\sim3\times10^2\ dm^3\ mol^{-1}\ s^{-1}$. The natural variable to represent the dependence of γ_{ss} on the acid content of H_2SO_4 is the activity of H_2O over the liquid at temperature (a_{H_2O}) resulting in a smooth curve of γ_{ss} as a function of a_{H_2O} given by $\gamma_{ss}=0.5(a_{H_2O})^2$, where a_{H_2O} is defined as the ratio of the equilibrium H_2O vapor pressure over the given H_2SO_4-H_2O liquid and the vapor pressure of supercooled water at the same temperature. This simple relationship has been shown to hold for $a_{H_2O} \geqslant 0.05$.

(f) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of $ClONO_2$ in the presence of HNO_3 and other reactants at characteristic densities of 10^{10} to 10^{11} molecule cm^{-3}. The cryogenic deposits were characterized by their vapor pressures of H_2O and HNO_3 detected by an ion-molecule reaction with F_2^- for H_2O and with F^- or SF_6^- for HNO_3, respectively. The frozen sulfuric acid surfaces were prepared by freezing a small amount of 57.7% H_2SO_4 (tetrahydrate) on the inside of the flow tube wall. The NAT layer was grown on a 0.5 μm thick H_2O ice undercoat on which a 0.05 μm thick NAT layer was deposited by flowing HNO_3 at 10^{-6} Torr. Subsequently the ice undercoat was sublimed off. The uptake coefficients were measured by monitoring the decrease of $ClONO_2$ with residence time. The results were obtained as a function of rh which was varied by adjusting the temperature of the frozen phase at a constant H_2O flow rate of 0.25 mTorr or by changing the H_2O flow rate at constant temperature to result in a range 10–90% rh. The uptake coefficients were strongly dependent on rh and were lower compared to uptake by liquid sulfuric acid.

(g) Fast flow reactor experiment coupled to a differentially pumped electron impact quadrupole MS using modulated molecular beam sampling. Two different flow tubes of 2.2 and 2.8 cm inner diameter were used, and the pressure was in the range 0.5–2 Torr. Corrections to the uptake coefficients owing to competitive gas phase diffusion amounted to 10% for $\gamma < 1\times10^{-2}$ and up to a factor of four for $\gamma > 0.2$. The liquid solution of SAT (57.5% H_2SO_4-H_2O) was applied to the inner wall of the flow tube as a film of $\geqslant 0.1$ mm thickness and was quickly cooled to temperatures around 195 K. The thermodynamic state of the SAT sample was controlled by setting the vapor pressure of H_2O, either H_2O-rich (approaching 100% rh) or H_2SO_4-rich at constant temperature or selecting the temperature at constant $p(H_2O)$. Ice films were deposited from the vapor phase at 195 K and attained a thickness of 15–25 mm. The rate law for both the decrease of $ClONO_2$ and the increase of HOCl were unimolecular in the range of concentrations examined and resulted in identical γ values. A fraction of HOCl remained adsorbed on the SAT surface so that a lower limit of the HOCl yield of 0.5 could be obtained. The uptake coefficient decreases from a value of 1.6×10^{-2} at close to 100% rh by almost two orders of magnitude to 5×10^{-4} at low rh as a function of decreasing $p(H_2O)$. The dependence of γ on $p(H_2O)$ (Torr) and on temperature (K) is conveniently expressed in parametric form: $\log\gamma=\{10.12+5.75\log[p(H_2O)]+0.62\log^2[p(H_2O)]\}$ for $T=195$ K, $p_{ClONO_2}=(3-5)\times10^{-8}$ Torr, $p(H_2O)=4\times10^{-5}$ to 5.6×10^{-4} Torr; $\log\gamma=\{318.67-3.13\log T+0.0076\log T\}$ for T in the range 192–206 K, $p_{ClONO_2}=(2-4)\times10^{-8}$ Torr and $p(H_2O)=3.4\times10^{-4}$ Torr. The latter expression includes the change in the thermodynamic state of the SAT surface.

(h) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of $ClONO_2$ in the presence of HNO_3 and other reactants at characteristic densities of 10^9 to 10^{11} molecule cm^{-3}. At high values of the uptake coefficient ($\gamma\geqslant0.1$) significant corrections for diffusion had to be made using calculated diffusion coefficients for the reactants in He. The primary observable is a first-order loss rate coefficient from which γ is calculated taking into account the diffusion correction and the corrected gas-wall collision frequency in the presence of a reactive surface. Rapid saturation of the ice surface for $ClONO_2$ uptake was observed, usually within minutes at concentrations as low as 2×10^9 molecule cm^{-3}. NAT was prepared *in situ* by converting N_2O_5 into HNO_3 on the ice surface well past saturation. The HNO_3 vapor detected at the downstream end of the flow tube was consistent within a factor of two with the expected vapor pressure over NAT-HNO_3-in-ice solid solution near 201 K. From the N_2O_5 taken up by the cryogenic substrate a 1 to 2 monolayer $[(2-4)\times10^{14}\ HNO_3\ cm^{-2}]$ thick NAT layer was inferred. No information regarding the saturation behavior of γ on the NAT surface is available. The relevant surface corresponds to the geometric area as an increase of the ice mass by a factor of 5 to 10 had no noticeable effect on γ.

(i) Ice-coated flow tube using electron-impact MS with ion-counting. The substrates were prepared by bubbling He through a HNO_3-H_2O solution and subsequently condensing the mixture (NAT films) at 196 K, resulting in film thicknesses of 70 μm. The surface areas and bulk densities of condensed films were measured *ex situ* in addition to the measurement of their FTIR absorption spectra. The reported data were corrected for external diffusion (important for large values of γ) using estimated diffusion coefficients in He as well as for pore diffusion (important for small values of γ) using a (semiquantitative) two-site surface reaction model: ice and NAT films were weighted according to their corresponding mass fractions. The characteristic pressures of $ClONO_2$ were in the range 8×10^{-5} Torr and the values given in the Table correspond to the fitted parameters for the pure phases of ice and stoichiometric NAT even though only NAT samples of varying compositions were used (37.6%–55.2% HNO_3-H_2O). The measured values of γ on samples of varying HNO_3-NAT composition, corrected for external diffusion, were in the range 10^{-3}–10^{-5}. Under the given experimental conditions the cryogenic surface saturated within a few minutes so that the results obtained within the first minute were retained. HOCl was detected as a reaction product although not used quantitatively.

(j) For experimental details see under Comment (h). These experiments were designed to investigate the influence of the thickness of the substrate on γ. The values for γ given in the Table correspond to a thickness of 10 μm where one can expect a coherent coat of substrate deposited from the vapor phase. The value for γ varied by a factor of no more than three and 1.5 for NAT and pure ice, respectively, when the thickness was varied from 2 to 20 μm. The conclusion was that there is no significant dependence of γ on thickness. In these experiments the stoichiometry of the reaction was confirmed by direct observation of HOCl at densities of $ClONO_2$ ranging from 4×10^9 to 7×10^{10} molecule cm^{-3} (lower limit of 50% for HOCl with respect to $ClONO_2$ consumed). However, the HOCl signal did not appear instantaneously after exposure of $ClONO_2$ to the ice surface. It therefore arises from adsorption of HOCl on ice and subsequent desorption. No such adsorption of HOCl was detected on NAT surfaces. An upper limit of 5% was set for the formation of Cl_2O. The temperature dependence of γ for $ClONO_2$ uptake on NAT corresponds to an activation energy of 24 kJ mol^{-1}: the availability of the H_2O molecules that are bound to HNO_3 in NAT increases with increasing temperature so they more readily support the hydrolysis of $ClONO_2$.

(k) Uptake experiment in an ice-coated flow tube using electron-impact quadrupole MS equipped with a closed ion-source. Uptake of $ClONO_2$ on NAT with careful control of the thermodynamic surface state of the cryogenic substrate with pressures of $ClONO_2$ ranging from $(2-20)\times10^{-6}$ Torr. The NAT films were prepared starting from 10 mm thick ice films that were exposed to small pressures of HNO_3 over long periods of time resulting in a 0.1 mm thick NAT layer on top of the ice film. Both the decay of $ClONO_2$ monitored at m/e 46 and the generation of HOCl observed at m/e 52 gave identical results. The uptake was studied on a number of NAT films ranging from HNO_3-rich $[p(H_2O)=4\times10^{-4}$ Torr, $\gamma=5\times10^{-5}]$ to H_2O-rich NAT $[p(H_2O)=1.5\times10^{-3}$ Torr, identical to the vapor pressure of ice at 202 K], $\gamma=2.0\times10^{-3}$. The reaction probability expressed as γ is a strong function of the thermodynamic state of the NAT surface. However, the experiments were conducted at pressures of $ClONO_2$ high enough to saturate a pure ice surface within the observation period. For these reference experiments identical values for γ were obtained ($\gamma=2.0\times10^{-3}$ at p_{ClONO_2} of 6×10^{-6} Torr).

(l) For experimental details see under Comments (h) and (j). This study was undertaken to supplement the original work on ice and nitric-acid doped (NAT) surfaces to further confirm the independence of the measured uptake coefficients on the substrate thickness.

(m) Uptake experiment in a two-chamber Knudsen cell using modulated molecular beam electron-impact MS. The uptake coefficient γ of $ClONO_2$ on pure ice prepared *in situ* by vapor deposition was measured at typical pressures $p_{ClONO_2}=0.02$ mTorr, $p(H_2O)=1.4$ mTorr by monitoring the decrease of the MS signal at m/e 46. HOCl and Cl_2O were confirmed as gas phase products, and HNO_3 was detected after warming up the ice that had undergone reaction with $ClONO_2$ to at least 217 K. The $ClONO_2$ sample had a significant impurity of Cl_2 and a lesser one of Cl_2O. Similar qualitative results were reported for $ClONO_2$ uptake on HNO_3-H_2O cryogenic surfaces that were co-condensed in the appropriate ratios before the uptake experiments. For HNO_3:H_2O mole ratios of 2:1 and 1:2, no reaction (observation of HOCl) was reported. However, for a 1:4.5 mole ratio, ''abundant'' formation of HOCl was reported essentially pointing to an identical situation with respect to reaction on pure ice.

(n) Fast flow tube reactor with electron-impact MS sampling. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total). The standard deviation of γ shown in the Table represents the uncertainty in the estimation of the diffusion coefficient of $ClONO_2$ in He at 200 K. HOCl was confirmed as the sole reaction product released into the gas phase.

(o) Uptake experiment in a flow reactor coupled to a differentially pumped electron-impact quadrupole MS. The total pressure was 0.4 Torr He, the active (cooled) surface was 183 cm^2 and the temperature was 188 ± 0.5 K. The ice film was deposited from water vapor saturated He to thicknesses ranging from 3.7 to 34.7 μm, which were both calculated and calibrated gravimetrically. The morphology of the ice films were layers of μm-sized granules whose internal surface was measured using BET gas adsorption measurements. In view of the buildup of HNO_3 on the ice substrate, minimum $ClONO_2$ concentrations were used ($p_{ClONO_2}=1.4\times10^{-7}$ Torr). The observation of the $ClONO_2$ decay led to an average uptake coefficient of 0.03 on thin ice films (≤4 μm thick) and of 0.13 on thick ice films (≤34.1 μm thick). The results based on the observation of the HOCl growth corresponded to smaller values of γ_{ss} because of the possible surface deactivation by the product HNO_3. Therefore the obtained values, which were corrected for gas-phase diffusion, are regarded as lower limits to the true uptake coefficients.

Preferred Values

The uptake coefficient on *liquid* H_2SO_4-H_2O around 220 K depends on the H_2O activity of the mixture and can be described by the following expression: $\log\gamma=\{1.84-0.075(\%H_2SO_4)\}$ (±20%). This expression is valid for the range of 40 to 80% H_2SO_4-H_2O mixtures and spans two and a half orders of magnitude in γ. Although this expression only applies to one temperature, there are indications that the temperature dependence of γ may be much weaker than the dependence on H_2O activity. This behavior is in marked contrast to that for the hydrolysis of N_2O_5 in sulfuric acid which is independent of sulfuric acid concentration over the same range. The γ values for *frozen* sulfuric acid corresponding to SAT (57.5% $H_2SO_4H_2O$) strongly depend on the thermodynamic state of the SAT surface. Typically, γ varies by almost two orders of magnitude at 195 K, namely from 1.6×10^{-2} to 5×10^{-4} when the rh is decreased from 100% to less than 1%. There are indications that γ increases with decreasing temperature at high rh. For frozen SAT samples at low relative humidity and $T=200$ K, the uptake is slowed down up to a factor of 40 relative to a liquid sample probably because of H_2O depletion or HNO_3 accumulation on the surface.

The uptake coefficient on NAT-like substrates at 190 K is on the order of 2×10^{-3}, similar to that for uptake on frozen SAT, and decreases by a factor of ten with decreasing rh from 90 to 25% probably due to H_2O depletion on the surface.

On water ice γ seems to be larger than on the other frozen surfaces, of the order of 0.1. This experiment seems to be prone to surface saturation effects.

The uptake coefficient for frozen surfaces seems to decrease in the following order: ice>SAT (H_2O-rich)>NAT (H_2O-rich). The thermodynamic state of the SAT and NAT surface corresponds to a high value of rh.

References

[1] M. J. Rossi, R. Malhotra, and D. M. Golden, Geophys. Res. Lett. **14**, 127 (1987).

[2] M. A. Tolbert, M. J. Rossi, and D. M. Golden, Geophys. Res. Lett. **15**, 847 (1988).

[3] D. R. Hanson and A. R. Ravishankara, J. Geophys. Res. **96**, 17307 (1991).

[4] D. M. Golden, J. A. Manion, C. M. Reihs, and M. A. Tolbert, in *CHEMRAWN VII: Chemistry of the Atmosphere: The Impact of Global Change*, edited by J. G. Calvert (Oxford University Press, New York, 1992).

[5] L. R. Williams, J. A. Manion, D. M. Golden, and M. A. Tolbert, J. Appl. Meteorol. **33**, 785 (1994).

[6] J. A. Manion, C. M. Fittschen, D. M. Golden, L. R. Williams, and M. A. Tolbert, Isr. J. Chem. **34**, 355 (1994).

[7] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **98**, 5728 (1994).

[8] D. R. Hanson and A. R. Ravishankara, J. Geophys. Res. **98**, 22931 (1993).

[9] R. Zhang, J. T. Jayne, and M. J. Molina, J. Phys. Chem. **98**, 867 (1994).

[10] D. R. Hanson and A. R. Ravishankara, J. Geophys. Res. **96**, 5081 (1991).

[11] M.-T. Leu, S. B. Moore, and L. F. Keyser, J. Phys. Chem. **95**, 7763 (1991).

[12] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **96**, 2682 (1992).

[13] J. P. D. Abbatt and M. J. Molina, J. Phys. Chem. **96**, 7674 (1992).

[14] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **97**, 2802 (1993).

[15] M. A. Tolbert, M. J. Rossi, R. Malhotra, and D. M. Golden, Science **238**, 1258 (1987).

[16] M.-T. Leu, Geophys. Res. Lett. **15**, 17 (1988).

[17] L. T. Chu, M.-T. Leu, and L. F. Keyser, J. Phys. Chem. **97**, 12798 (1993).

$ClONO_2 + HCl \rightarrow HNO_3 + Cl_2$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
	Sulfate/H_2SO_4 (liquid) Substrates				
γ_{ss}	3.0×10^{-3}	65% H_2SO_4	210	Tolbert, Rossi, and Golden, 1988[1]	(a)
γ_{ss}	2.0×10^{-2}	40% H_2SO_4	218±3	Hanson and Ravishankara, 1991[2]	(b)
	2.0×10^{-4}	60% H_2SO_4	218±3		
	$<10^{-4}$	65% H_2SO_4	218±3		
	$<2.0\times10^{-5}$	70% H_2SO_4	218±3		
	$<2.0\times10^{-5}$	75% H_2SO_4	218±3		
γ_{ss}	3.8×10^{-2}	46.6% H_2SO_4, liquid, $<10^{-4}$ M HCl	202	Hanson and Ravishankara, 1994[3]	(c)
	1.1×10^{-1}	46.6% H_2SO_4, liquid, HCl$=10^{-3}$ M	202		
	3.0×10^{-1}	46.6% H_2SO_4, liquid, HCl$=6\times10^{-3}$M	202		
	Sulfate/H_2SO_4 (solid) Substrates				
γ_{ss}	1.25×10^{-1}	57.5% H_2SO_4	192	Hanson and Ravishankara, 1993[4]	
	2.4×10^{-4}	57.5% H_2SO_4	205		(d)
γ_{ss}	$(1.2\pm0.3)\times10^{-1}$	SAT, H_2O-rich, 100% rh	195	Zhang, Jayne, and Molina, 1994[5]	
	$(7.0\pm2.0)\times10^{-4}$	SAT, H_2SO_4-rich, 0.7% rh	195		(e)
	HNO_3-H_2O Substrates				
γ_{ss}	$0.3^{+0.7}_{-0.1}$	NAT film	200	Hanson and Ravishankara, 1991[6]	(f)
γ_{ss}	$(2.7\pm0.4)\times10^{-1}$	NAT film	196	Leu, Moore, and Keyser, 1991[7]	(g)
γ_{ss}	$0.3^{+0.7}_{-0.1}$	NAT film	191	Hanson and Ravishankara, 1992[8]	(h)
γ_{ss}	$(3.0\pm1.0)\times10^{-3}$	HNO_3-rich NAT	202	Abbatt and Molina, 1992[9]	(i)
	$\geqslant2.0\times10^{-1}$	H_2O-rich NAT	202		
γ_{ss}	2.3×10^{-1}	NAT, $p_{HCl}=5\times10^{-8}$ Torr, 90% rh	190	Hanson and Ravishankara, 1993[4]	(j)
	2.0×10^{-1}	NAT, $p_{HCl}=(3-4)\times10^{-7}$ Torr, 90% rh	190		
	3.0×10^{-2}	NAT, $p_{HCl}=(3-4)\times10^{-7}$ Torr, 30% rh	197		
	H_2O (solid)				
γ_{ss}	$0.27^{+0.73}_{-0.13}$	HCl-H_2O film	200	Leu, 1988[10]	(k)
γ_{ss}	$0.3^{+0.7}_{-0.1}$	ice film	191	Hanson and Ravishankara, 1992[8]	(h)
γ_{ss}	$(2.7\pm1.9)\times10^{-1}$	10.4 mm thick ice film	188	Chu, Leu, and Keyser, 1993[11]	(l)

Comments

(a) Uptake experiment in a Knudsen cell flow reactor coupled to a modulated molecular beam sampled electron-impact MS. The bulk substrate (1–5 mL) was cooled slowly to temperatures of 210 to 230 K. The H_2SO_4 concentration in the bulk was obtained by dilution from 96.5% H_2SO_4 and was chosen to reflect the sulfuric acid aerosol concentration under stratospheric conditions, that is in the temperature range 210 to 230 K and a vapor pressure of 4×10^{-4} Torr (±30%) which was the measured steady-state vapor pressure in the Knudsen cell. Before the $ClONO_2$ uptake experiment, the 65%

H_2SO_4-H_2O solution was exposed to 1.3 mTorr of HCl for an hour (estimated mole fraction ratio HCl:$H_2O=2\times10^{-4}$) after which the bulk cryogenic phase was exposed to $ClONO_2$ at typical pressures of 4.8 mTorr. The measured γ values were measured under steady-state conditions with $ClONO_2$ (monitored at m/e 46) and are very similar to the ones measured in uptake experiments without HCl by the same authors (see Data Sheet for $ClONO_2$ + H_2O). Gaseous reaction products HOCl (m/e 51/53), Cl_2 (m/e 70/72/74), and Cl_2O (m/e 86/88/90) were observed as was condensed phase HNO_3 through desorption experiments. More than 85% of the HCl was recoverable as Cl_2 from the 65% H_2SO_4 solution at 210 K. It is obvious that in addition to the title reaction, the reaction $ClONO_2$ + H_2O is occurring simultaneously.

(b) Uptake experiment on a wetted-wall flow tube with chemical ionization MS detection. This method allows selective detection of $ClONO_2$ in the presence of HNO_3 and other reactants at characteristic densities of 10^{10} to 10^{11} molecule cm^{-3}. The cold aqueous solution of H_2SO_4 (40 to 75%, T=215–230 K) was flowed down the walls of the flow tube with a liquid film residence time of 20–30 s. $p(H_2O)$ was generally around 1 mTorr. The HCl concentration for the experiments on the 40% solution was 2×10^{11} molecule cm^{-3}, that for the 60 to 75% solution was in the range $(1-3)\times10^{10}$ molecule cm^{-3}. The error limits are reported to be ($^{+100}_{-50}$%) except for the 40 and the 60% solution, and Cl_2 was confirmed as a reaction product. The uptake of $ClONO_2$ in the presence of HCl was not accelerated compared to experiments without HCl. The authors suggest that this reaction occurs in the liquid phase with the rates controlled by the solubilities of the reactants. The reaction probability (γ) for the title reaction is suggested to be at most 10% of the value of γ for the reaction $ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$. A number of experiments were performed at high HCl concentrations, with the result that γ was significantly enhanced at comparable $ClONO_2$ concentrations: for a 60% solution γ was 2×10^{-4} (215 K), 0.006 (215 K), and ~0.01 (238 K) for HCl concentrations of 2×10^{10}, 7×10^{12}, and $\sim5\times10^{12}$ molecule cm^{-3}, respectively.

(c) Uptake experiment in a laminar-flow tube of gas-phase $ClONO_2$ onto a quiescent liquid surface with chemical ionization detection MS as a partial pressure monitor. H_2SO_4 (46.6% to 65%) was applied as a cold liquid to the inner wall of the flow tube. The liquid H_2SO_4 was back-titrated after the uptake experiment, and the product HOCl was qualitatively detected only for the case of no added HCl. The HCl was either added to the liquid (46.6% and 51% H_2SO_4) or taken up from the gas phase (55.6, 57.5, 58.5, 59.8, and 65% H_2SO_4). The first-order loss rate coefficients were based on the disappearance of $ClONO_2$ and were ≥ 10 s^{-1}. No significant temperature dependence of the uptake coefficient in the temperature range 192 to 208 K was observed. The uptake coefficient increased with increasing p_{HCl} and increasing H_2O activity. The results can be summarized as follows: $1.0\times10^{-3}\leq\gamma$ ≤ 0.30 at 46.6 to 65% H_2SO_4, 8×10^{-9} to 8×10 Torr HCl and at T=202 K. $ClONO_2$ undergoes a competitive reaction with both HCl (k^{II}_{HCl}) and H_2O (hydrolysis, k^{I}_{0}). It was found from curve fitting that a surface-mediated reaction between Cl^- and $ClONO_2$ scaling with p_{HCl} had to be invoked in addition to the competitive bulk reactions. A two-parameter fit to the global data set revealed a slow hydrolysis reaction ($k^{I}_{0}\sim300$ dm^3 mol^{-1} s^{-1}) with k^{II}_{HCl} estimated to be at or close to its diffusion limit of $(1-3)\times10^7$ dm^3 mol^{-1} s^{-1}at 202 K and for 50% H_2SO_4-H_2O. The $ClONO_2$ uptake therefore does not vary linearly with p_{HCl}. An estimate within a factor of three is given for the solubility of $ClONO_2$ at 202 K and 60% acid (H =1000 mol dm^{-3} atm^{-1}).

(d) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of $ClONO_2$ in the presence of HNO_3 and other reactants at characteristic densities of 10^{10} to 10^{11} molecule cm^{-3}. The cryogenic deposits were characterized by their vapor pressure of H_2O detected by an ion-molecule reaction with F_2^-, whose decrease was monitored as a function of H_2O pressure. The sulfuric acid surfaces were prepared by freezing a small amount of 57.7% H_2SO_4 (tetrahydrate) on the inside of the flow tube wall. The results were obtained as a function of rh which was varied by adjusting the temperature of the frozen phase at a constant H_2O flow rate of 0.2 mTorr or by changing the H_2O flow rate at constant temperature to result in a range 10–90% rh. The HCl partial pressure was held at approximately 1.5×10^{-7} Torr, corresponding to 2–3 ppbv at 17 km and the water vapor pressure for the γ values given in the Table was 5×10^{-4} Torr. The uptake coefficients decreased markedly with decreasing rh and could be expressed as $\ln\gamma=(-0.636-0.4802\Delta T)$, where $\Delta T=T-189$. ΔT can be approximated by $T-T_{ice}$ where T_{ice} is the temperature of the ice point at a given partial pressure of water vapor and where $p(H_2O)<p_{ice}$. Because the uptake coefficient over frozen sulfate is identical to within experimental error to that over NAT [see Comment (k)], it is believed that rh is the dominant controlling factor for $ClONO_2$ uptake.

(e) Fast flow reactor experiment coupled to a differentially pumped electron impact quadrupole MS with molecular beam sampling. Two different flow tubes of 2.2 and 2.8 cm inner diameter were used, and the pressure was in the range 0.5–2 Torr. Corrections to the uptake coefficients arising from competitive gas-phase diffusion amounted to 10% for $\gamma<1\times10^{-2}$ and up to a factor of four for $\gamma>0.2$. The liquid solution of SAT (57.5% H_2SO_4-H_2O) was applied to the inner wall of the flow tube as a film of ≥ 0.1 mm thickness and was quickly cooled to temperatures around 195 K. The thermodynamic state of the SAT sample was controlled by setting the vapor pressure of H_2O, either H_2O-rich (approaching 100% rh) or H_2SO_4-rich at constant temperature or selecting the temperature at constant $p(H_2O)$. Ice films were deposited from the vapor phase at 195 K and attained a thickness of between 15–25 μm. The rate law for both the decrease of $ClONO_2$ and the increase of Cl_2, whose yield was measured to be 0.9 ± 0.1, were unimolecular in the range of concentrations examined and resulted in identical γ values. The HCl was always in excess of $ClONO_2$ and no HOCl was detected. The uptake coefficient decreases from a value of 1.2×10^{-1} at close to 100% rh by more than two orders of magnitude to 7×10^{-4} at low rh as a function of decreasing $p(H_2O)$. The dependence of γ on $p(H_2O)$ (Torr) and on temperature (K) is conveniently expressed in parametric form: $\log \gamma=[5.25+1.91 \log p(H_2O)]$ for $T=195$ K, $p_{ClONO_2}=(3-5)\times10^{-8}$ Torr, $p_{HCl}=(4-8)\times10^{-7}$ Torr, $p(H_2O)=4\times10^{-5}$ to 5.6×10^{-4} Torr; $\log \gamma=(175.74-1.59 \log T+0.0035 \log^2 T)$ for T in the range 195–206 K, $p_{ClONO_2}=(3-5)\times10^{-8}$ Torr, $p_{HCl}=(4-8)\times10^{-7}$ Torr, and $p(H_2O)=5.6\times10^{-4}$ Torr. The latter expression includes the change in the thermodynamic state of the SAT surface.

(f) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of $ClONO_2$ in the presence of HNO_3 and other reactants at characteristic densities of 10^9 to 10^{11} molecule cm^{-3}. At high values for the uptake coefficient ($\gamma \geq 0.1$), significant diffusion corrections had to be made using calculated diffusion coefficients for the reactants in He. The primary observable was a first-order loss rate coefficient from which γ was calculated taking into account the diffusion correction and the corrected gas-wall collision frequency in the presence of a reactive surface. NAT was prepared *in situ* by converting N_2O_5 into HNO_3 on the ice surface well past saturation. The HNO_3 vapor detected at the downstream end of the flow tube was consistent within a factor of two with the expected vapor pressure over NAT-HNO_3 in-ice solid solution near 201 K. From the N_2O_5 taken up by the cryogenic substrate a NAT film 1 to 2 monolayers thick [$(2-4)\times10^{14}$ HNO_3 cm^{-2}] was inferred. The first-order loss rate coefficient of $ClONO_2$ on pure ice in the presence of HCl was identical to that measured in the absence of HCl, thus indicating no preference for reaction of $ClONO_2$ with HCl over that with H_2O, presumably because γ is already close to one. For the uptake experiments on NAT the HCl concentration was set to twice that for $ClONO_2$, namely $(2-6)\times10^9$ molecule cm^{-3}. The reaction is limited by the availability of HCl as excess conditions must be maintained. However, no information on the possible saturation of γ is available. The relevant surface corresponds to the geometric area, as an increase of the ice mass by a factor of 5 to 10 had no noticeable effect on γ.

(g) Ice-coated flow tube using electron-impact MS with ion-counting as a diagnostic. The substrates were prepared by bubbling He through a HNO_3-H_2O solution and subsequently condensing the mixture (NAT films) at 196 K, resulting in film thicknesses of 70 μm. The surface areas and bulk densities of condensed films were measured *ex situ* in addition to the measurement of their FTIR absorption spectra. The reported data were corrected for external diffusion (important for large values of γ) using estimated diffusion coefficients in He. The characeristic pressures were: $p_{HCl}=0.2$ to 2 mTorr, $p_{ClONO_2}=8\times10^{-5}$ Torr. The measured values of γ were independent of the composition of HNO_3-H_2O in the range 41.8–60.4% and of the HCl content (0.0375%–3.91% HCl). The experiments were conducted at excess HCl over $ClONO_2$, no surface deactivation was observed and both $ClONO_2$ loss as well as Cl_2 appearance were used in the measurement of γ. The scatter in the data is largely given by the diffusion correction, and the authors give a corrected value of $\gamma=0.10\pm0.02$ if pore diffusion is taken into account.

(h) For experimental details see under Comment (f). Characteristic reactant concentrations were from 2×10^9 to 10^{10} molecule cm^{-3}. The experiments were designed to verify the identity of the reaction products. $ClONO_2$, HCl, and Cl_2 were monitored albeit not simultaneously. Under conditions of [HCl] > [$ClONO_2$], no saturation of the uptake of $ClONO_2$ and no HOCl were detected. It is suggested that the HOCl intermediate that is adsorbed on the ice undergoes a fast reaction with HCl. For the experiments on NAT the uptake of $ClONO_2$, HCl, and the formation of the reaction product Cl_2 were studied at constant HCl concentration (2×10^{10} molecule cm^{-3}) and varying $ClONO_2$ concentration ranging from 6×10^9 to 3×10^{10} molecule cm^{-3}. A first-order rate law for uptake of HCl and $ClONO_2$, as well as for the formation of Cl_2, were found. The authors argue in favor of a direct reaction between $ClONO_2$ and HCl rather than a reaction via the intermediate HOCl in view of the high value for γ. The low value for γ found for the reaction of $ClONO_2 + H_2O$ on NAT would virtually preclude the present result if this reaction were part of the overall reaction mechanism: $ClONO_2 + H_2O \rightarrow HOCl + HNO_3$, and $HOCl + HCl \rightarrow Cl_2 + H_2O$ (net reaction is the title reaction).

(i) Uptake experiment in an ice-coated flow tube using electron-impact quadrupole MS equipped with a closed ion-source. Uptake of $ClONO_2$ on NAT in the presence of a slight excess of HCl with careful control of the thermodynamic surface state of the cryogenic substrate with pressure of $ClONO_2$ ranging from $(1-9)\times10^{-6}$ Torr and HCl ranging from $(4-10)\times10^{-6}$ Torr. The NAT films were prepared starting from 10 μm thick ice films that were exposed to small pressures of HNO_3 over long periods of time resulting in a 0.1 μm thick NAT layer on top of the ice film. Both the Cl_2 product formation as well as the $ClONO_2$ decay was observed in order to measure the reaction probability (γ). Under conditions of slight excess of HCl, γ was measured as a function of $p(H_2O)$ from HNO_3-rich NAT to H_2O-rich NAT: for $p(H_2O)=2\times10^{-4}$ Torr (HNO_3-rich NAT), $\gamma=0.003$; and at the other extreme of the NAT existence curve [$p(H_2O)=1.5\times10^{-3}$ Torr, H_2O-rich], $\gamma=0.2$ was found. Additional experiments of the dependence of γ on p_{HCl} for HNO_3-rich NAT [$p(H_2O)=2.5\times10^{-4}$ Torr] resulted in a factor of four increase in γ (from 0.01 to 0.04) when p_{HCl} was increased from 1.5×10^{-5} to 8×10^{-5} Torr. At even higher pressures of HCl [$(1-2)\times10^{-4}$ Torr], $\gamma>0.5$ was measured due to the unlimited uptake of HCl into the molten surface phase of HCl-H_2O. Little HCl is taken up by HNO_3-rich NAT so that the resulting low surface concentration of HCl leads to small reaction probabilities.

(j) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of $ClONO_2$ and HCl in the presence of HNO_3 and other reactants at characteristic densities of 10^{10} to 10^{11} molecule cm^{-3}. The cryogenic deposits were characterized by their vapor pressures of H_2O and HNO_3 detected by an ion-molecule reaction with F_2^- for H_2O and with F^- or SF_6^- for HNO_3, respectively. The NAT layer was grown on a 0.5 mm thick H_2O ice undercoat on which a 0.05 μm thick NAT layer was deposited by flowing HNO_3 at 10^{-6} Torr. Subsequently the ice undercoat was sublimed off. The results were obtained as a function of relative humidity which was varied by adjusting the temperature of the frozen phase at a constant H_2O flow rate of 0.25 mTorr. In some instances NAD deposits were obtained that converted to NAT within an hour. The uptake coefficients on NAD were similar if not slightly higher than on NAT under identical conditions. The partial pressure of HCl was about twice that of $ClONO_2$ and the loss rate of $ClONO_2$ on NAT followed a first-order rate law. The uptake coefficients were only slightly dependent on the temperature and p_{HCl} but strongly decreasing with decreasing rh. The expression $1/\gamma=1/\gamma_{max}+1/A\exp(B\Delta T)$ described well the dependence of the uptake coefficients on temperature, and thus relative humidity. ΔT is defined as $T-190$, the departure of the temperature of interest from the ice point temperature at which rh is 100% at the chosen flow rate of H_2O [rh $=100p(H_2O)/p_{ice}(T)$], $A=0.7022$ and 2.2543, $B=-0.518$ and -0.558 for $p_{HCl}=5\times10^{-8}$ Torr and $(3-4)\times10^{-7}$ Torr, respectively.

(k) Fast flow tube reactor with electron-impact mass spectrometric sampling as a diagnostic. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total) together with HCl vapor to obtain mole fractions f_{HCl} in the range 0.37 to 7.1% relative to H_2O. The reaction probability γ increased from 0.06, the value obtained for the reaction $ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$ to a constant value of 0.27 independent of f_{HCl} for the range 1.5 to 7.1% (see Table). The standard deviation of the γ value shown in the Table represents the uncertainty in the estimation of the diffusion coefficient of $ClONO_2$ and HCl in He at 200 K. Cl_2 was confirmed as the sole reaction product released into the gas phase. For $f_{HCl}=0.37\%$, both Cl_2 and HOCl were observed. Moreover, evidence for fast diffusion of HCl across an amorphous ice layer has been obtained.

(l) Uptake experiment in a flow reactor coupled to a differentially pumped electron-impact quadrupole MS. The total pressure was 0.4 Torr He, the active (cooled) surface was 183 cm^2 and the temperature was 188 ±0.5 K. The ice film was deposited from water vapor saturated He to thicknesses ranging from 3.7 to 34.7 μm, which were both calculated and calibrated gravimetrically. The morphology of the ice films were layers of μm-sized granules whose internal surface was measured using BET gas adsorption measurments. A typical experimental sequence included conditioning of the ice film by a constant flow of HCl after which a flow of $ClONO_2$-saturated He was added to the flow tube. The concentration of HCl was always larger than that for $ClONO_2$ such that pseudo-first-order conditions prevailed. p_{ClONO_2} ranged from 6.5×10^{-8} to $\sim10^{-6}$ Torr and p_{HCl} from 1.6×10^{-7} to 2.3×10^{-6} Torr. The observation of the $ClONO_2$ decay led to an average uptake coefficient of 0.26 ± 0.19, and the monitoring of the growth of Cl_2 led to a value for γ_{ss} of 0.28 ± 0.18, the median of which is given in the Table. The results were independent of p_{ClONO_2}, p_{HCl}, and temperature within experimental variability, and all were corrected for gas-phase diffusion. This correction amounted to a factor exceeding ten in some cases. Taking into account a structural model for the ice substrate, a value of $\gamma_{ss}=0.10\pm0.08$ was obtained which is approximately a factor of 2.6 smaller than the value based on the geometrical (external) surface. The surface roughness rather than the porosity of the film is seen as the principal parameter being responsible for the reduction of the measured γ_{ss}. The Cl_2 yield based on the $ClONO_2$ reacted was measured as 1.2 ± 0.2 under excess HCl condition.

Preferred Values

The uptake coefficient for *liquid* H_2SO_4-H_2O at $T=220$ K is a strong function of the water activity in analogy to the results for the reaction $ClONO_2 + H_2O$. For 40% H_2SO_4-H_2O γ is lower by a factor of four and for 75% H_2SO_4-H_2O lower by a factor of 10 in comparison to the reaction with H_2O on the same bulk substrates. The total variation of γ with water activity spans a range of three orders of magnitude. The uptake coefficient scales with the HCl partial pressure attaining a γ value of 0.3 at 10^{-4} Torr HCl at 202 K. On *frozen* SAT, γ seems to be similar to the one for liquid sulfuric acid. However, γ strongly depends on the thermodynamic state of the SAT surface: Its value decreases by more than two orders of magnitude at 195 K, from 1.2×10^{-1} at 100% rh to 7×10^{-4} at low rh. There are indications of an increase of γ with decreasing temperature for H_2O-rich SAT surfaces (high rh).

On NAT-like and H_2O-rich NAT substrates the uptake coefficient is found to be large, on the order of 0.3 at $T = 190$ K. It decreases significantly for substrates at low rh or correspondingly for HNO_3-rich conditions by up to two orders of magnitude.

On a water ice substrate the uptake coefficient is found to be large, on the order of 0.1 to 0.3 at 190 K.

References

[1] M. A. Tolbert, M. J. Rossi, and D. M. Golden, Geophys. Res. Lett. **15**, 847 (1988).

[2] D. R. Hanson and A. R. Ravishankara, J. Geophys. Res. **96**, 17307 (1991a).

[3] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **98**, 5728 (1994).

[4] D. R. Hanson and A. R. Ravishankara, J. Geophys. Res. **98**, 22931 (1993).

[5] R. Zhang, J. T. Jayne, and M. J. Molina, J. Phys. Chem. **98**, 867 (1994).

[6] D. R. Hanson and A. R. Ravishankara, J. Geophys. Res. **96**, 5081 (1991).

[7] M.-T. Leu, S. B. Moore, and L. F. Keyser, J. Phys. Chem. **95**, 7763 (1991).

[8] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **96**, 2682 (1992).

[9] J. P. D. Abbatt and M. J. Molina, J. Phys. Chem. **96**, 7674 (1992).

[10] M.-T. Leu, Geophys. Res. Lett. **15**, 17 (1988).

[11] L. T. Chu, M.-T. Leu, and L. F. Keyser, J. Phys. Chem. **97**, 12798 (1993).

$ClONO_2 + HBr \rightarrow BrCl + HNO_3$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\sim 1.0 \times 10^{-2}$	cold Pyrex	201	Hanson and Ravishankara, 1992[1]	(a)
	$\geqslant 3.0 \times 10^{-1}$	cold Pyrex at 50% rh, H_2O-ice, NAT	201		

Comments

(a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS with selective detection of HBr and other halogen containing reactants and products. Ice layers 2–10 μm thick were condensed from the vapor phase onto the cold flow tube wall and HNO_3-treated ice was defined as NAT under the used experimental conditions. On cold Pyrex both the decrease of $ClONO_2$ and HBr as well as the increase in BrCl were observed. The reactive uptake coefficient scales with the amount of adsorbed HBr: no reaction was observed at 220 K, and no uptake of $ClONO_2$ could be observed in the absence of HBr. On cold Pyrex at 50% rh an efficient reaction with $\gamma_{ss} \geqslant 0.3$ could be observed under conditions of excess $ClONO_2$. However, a smaller yield of BrCl was observed owing to the fast secondary reaction $BrCl + HBr \rightarrow HCl + Br_2$. The authors do not exclude the possibility that the title reaction might occur through formation of $BrONO_2 + HCl$ with a subsequent rapid formation of $Br_2 + HNO_3$. No difference in reactivity was found between pure ice and "NAT," presumably because the former was rapidly converted into NAT owing to the deposition of HNO_3 from the title reaction. The reaction did not show any signs of saturation, and identical results were obtained for γ_{ss} measured from the disappearance of either $ClONO_2$ or HBr. At excess HBr no BrCl was observed due to the fast secondary reaction between BrCl and HBr.

References

[1] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **96**, 9441 (1992).

$ClONO_2 + HF \rightarrow$ products

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\leqslant 1.0 \times 10^{-2}$	H_2O-ice, NAT	201	Hanson and Ravishankara, 1992[1]	(a)

Comments

(a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS with selective detection of HBr and other halogen containing reactants and products. Ice layers 2–10 μm thick were condensed from the vapor phase onto the cold flow tube wall and HNO_3-treated ice was defined as NAT under the experimental conditions used. On pure H_2O-ice or NAT into which the pure ice substrate was converted only the known reaction of $ClONO_2 + H_2O$ was observed with $\gamma_{ss}=0.015$ as measured from the formation of HOCl. It accounted for 50%–75% of the $ClONO_2$ lost. Even at high initial HF concentrations of the order of 2×10^{13} molecule cm^{-3} no new products were detected. The listed value for γ_{ss} represents a conservative upper limit with the most probable value being a factor of 10^4 lower under stratospheric conditions. HF itself was not observed to interact measurably with the ice substrate.

References

[1] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **96**, 9441 (1994).

$ClONO_2 + NaCl \rightarrow Cl_2 + NaNO_3$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$(4.6\pm3.1)\times10^{-3}$	dry salt, baked	296	Timonen *et al.*, 1994[1]	(a)
	$(6.7\pm3.2)\times10^{-3}$		225		

Comments

(a) Uptake experiment in a flow reactor coupled to a differentially pumped electron-impact quadrupole MS. The total pressure in the flow tube was 0.3 Torr He. Both the decrease of $ClONO_2$ monitored at m/e 46 as well as the increase of Cl_2 monitored at m/e 70 were used to calculate the uptake coefficient. The internal surface of the dry NaCl sample ground to an average size of 4 μm was determined in separate experiments and agrees with the internal surface calculated from average dimensions observed in SEM pictures. The measured uptake coefficient was corrected for radial diffusion (% level) and for the uptake on the external surface of deeper layers of NaCl exposed to the gas phase according to a chemical engineering model applied by the authors. This latter correction decreases the observed value for γ_{ss} by a factor of 7 to 8, with a global uncertainty of a factor of 2 associated with uncertainties in the model parameters used to reduce the raw values of γ_{ss}. The values displayed in the above Table do not correspond to the measured uptake coefficients, but reflect the results after theoretical treatment. The $ClONO_2$ concentration varied from 2.5×10^{-8} to 1.9×10^{-6} Torr and the uptake coefficient was independent of the $ClONO_2$ pressure. The dose of $ClONO_2$ to saturation corresponds to adsorption of 18 monolayers at 296 K and to one monolayer at 225 K. The addition of H_2O vapor in the range 5.7×10^{-5}–3×10^{-4} Torr decreased γ_{ss} by approximately 10% at both temperatures. With increasing H_2O concentration, increasing amounts of HNO_3 and HOCl but no HCl were observed.

References

[1] R. S. Timonen, L. T. Chu, M.-T. Leu, and L. F. Keyser, J. Phys. Chem. **98**, 9509 (1994).

$HOCl + HCl \rightarrow Cl_2 + H_2O$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
	Sulfate/H_2SO_4 (liquid) Substrates				
γ_{HCl}	6.0×10^{-3}	60% H_2SO_4	215	Hanson and Ravishankara, 1991[1]	(a)
γ_{HOCl}	1.0×10^{-3}	60% H_2SO_4	263		
γ_{HOCl}	$(2.0\pm0.5)\times10^{-2}\leqslant\gamma\leqslant(1.8\pm0.8)\times10^{-1}$	60% H_2SO_4	200–220	Hanson and Ravishankara, 1993[2]	(b)
	HNO_3–H_2O Substrates				
γ_{ss}	$(1.0\pm0.25)\times10^{-1}$	NAT	191	Hanson and Ravishankara, 1992[3]	(c)
γ_{ss}	1.7×10^{-1}	H_2O-rich NAT, 100% rh	202	Abbatt and Molina, 1992[4]	(d)
	2.0×10^{-3}	HNO_3-rich NAT, 17.8% rh	202		
	H_2O (solid) Substrates				
γ_{ss}	$\geqslant0.3^{+0.7}_{-0.1}$	ice film	191	Hanson and Ravishankara, 1992[3]	(c)
γ_{ss}	$(1.6\pm1.0)\times10^{-1}$	ice film	202	Abbatt and Molina, 1992[4]	(d)
	$0.24^{+0.5}_{-0.15}$				
		ice film	195		
γ_{ss}	$(3.4\pm2.0)\times10^{-1}$	19.4 μm thick ice film	188	Chu, Leu, and Keyser, 1993[5]	(e)

Comments

(a) Uptake experiment in a wetted-wall flow tube using chemical ionization MS detection. This method allows selective detection of reactants at characteristic densities of 10^{10} to 10^{11} molecule cm^{-3}. The cold aqueous solution of H_2SO_4 (60%, T=215 and 263 K) was flowing down the walls of the flow tube with a liquid film residence time of 20–30 s. $p(H_2O)$ was generally around 1 mTorr. HOCl was generated through the reaction $ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$ over 60% H_2SO_4. The uptake coefficient for HCl in the presence of HOCl was significantly larger than that in the absence of HOCl (see HCl data sheet, $\gamma=4\times10^{-4}$) in part due to the large reactant concentrations: $[ClONO_2]=10^{12}$ molecule cm^{-3} and $[HCl]=3\times10^{11}$ molecule cm^{-3}. The uptake coefficient γ_{HOCl} has been measured at $[ClONO_2]=10^{11}$ molecule cm^{-3} and $[HCl]=2\times10^{11}$ molecule cm^{-3}, Cl_2 has been confirmed as a reaction product. It is thought that the title reaction is a condensed phase reaction with a rate coefficient of 10^4 to 10^5 dm^3 mol^{-1} s^{-1}.

(b) Time-dependent uptake experiment in a flow tube (0.4 to 2 Torr He) coupled to a chemical ionization MS. The liquid H_2SO_4 was either applied to the internal wall of the flow tube with subsequent determination of the acid content by titration (59.6%), or the liquid sample was in a boat container lying on the bottom of the horizontal flow tube. H_2O vapor was added to the He carrier to control the H_2SO_4 concentration. HOCl came from three sources: (1) entrainment from a solid $Ca(OCl)_2$ sample exposed to H_2O and HCl, (2) from the heterogeneous reaction of $ClONO_2$ on the substrate to be studied, and (3) from an equilibrium mixture of Cl_2O (1 Torr) and H_2O (15 Torr). Pseudo-first-order conditions prevailed during the time-dependent uptake measurements performed in the temperature range 200–220 K with $[HCl]_0 \gg [HOCl]_0$. The values for γ increase with p_{HCl} ranging from 2.3×10^{-7} to 3.6×10^{-5} Torr. The experimental conditions were chosen such that the chloride concentrations in the liquid phase were $\geq 10^{-5}$ mol dm^{-3} and the HOCl uptake coefficient was independent of $[HOCl]_0$. The bimolecular rate coefficient for the title reaction in 60% H_2SO_4 and for the temperature range 200–220 K was found to be 1.6×10^5 dm^3 mol^{-1} s^{-1} with a factor of two uncertainty. Solubilities (effective Henry's law constants for HCl, H^*_{HCl}, and H_{HOCl}) and diffusion constants for the liquid phase of HCl (D_l) were obtained from time dependent uptake measurements of HCl and HOCl and "direct" determinations of solubilities for HCl from pseudostatic, that is low flow rate experiments. The separation of the factors in $H^*(D_l)^{1/2}$ resulting from time-dependent uptake experiments was obtained through direct measurement of H^*_{HCl} for some cases thus obtaining temperature-dependent values for both H^*_{HCl} and D_l. It was assumed D_l was identical for both HCl and HOCl and that it was independent of acid concentration in the range 45–60%.

(c) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of reactants at characteristic densities of 10^9 to 10^{11} molecule cm^{-3}. At high values of the uptake coefficient ($\gamma \geq 0.1$) significant diffusion corrections had to be made using calculated diffusion coefficients for the reactants in He. The source of HOCl was the reaction HCl + $Ca(ClO)_2$ for the ice experiments, and an equilibrium mixture of Cl_2O + H_2O. The decay of HCl and HOCl resulted in identical decay rates for $[HOCl]=2\times10^9$ molecule cm^{-3} and [HCl] ranging from 2×10^9 to 2×10^{10} molecule cm^{-3}. In separate experiments, Cl_2 was identified as a reaction product. No saturation effects were observed in keeping with the volatility of Cl_2 over ice surfaces. For the NAT experiments the concentrations were $[HOCl]=[HCl]=10^{10}$ molecule cm^{-3}.

(d) Uptake experiment in an ice-coated flow tube using electron-impact quadrupole MS equipped with a closed ion-source as a probe. The uptake of HOCl in the presence of HCl (in excess by a factor of two or so) was time-independent and therefore not saturable. The reaction product on ice and NAT has been confirmed to be Cl_2, with a yield of 0.87±0.20. On ice and for [HCl] > [HOCl] a negative temperature dependence of γ has been observed: γ increases from 0.16 to 0.24 when the temperature drops from 202 to 195 K (see Table). There is an indication that γ increases slightly with increasing HCl pressure (preliminary finding). As the H_2O partial pressure drops from 1.7 mTorr at 202 K (the equilibrium vapor pressure for pure H_2O ice) to 0.8 mTorr and 0.3 mTorr, γ drops precipitously from 0.13 to 0.07 and reaching a value of 0.002 for HNO_3-rich NAT. At 195 K, γ was found to be 0.18 ±0.10 at H_2O pressures greater than 0.2 mTorr. (The equilibrium vapor pressure of H_2O over ice at 195 K is 0.56 mTorr.) This last value for γ is at least somewhat unexpected as the water vapor pressure of 0.2 mTorr should favor the formation of NAT in the midrange between H_2O-rich and HNO_3 rich and we therefore expect a smaller value for γ.

(e) Uptake experiment in a flow reactor coupled to a differentially pumped electron-impact quadrupole MS. The total pressure was 0.4 Torr He, the active (cooled) surface was 183 cm^2, and the temperature was 188 ±0.5 K. The ice film was deposited from water vapor saturated He to thicknesses ranging from 3.7 to 34.7 μm, which were both calculated and calibrated gravimetrically. The morphology of the ice films were layers of μ-sized granules whose internal surface was measured using BET gas adsorption measurements. A typical experimental sequence included conditioning of the ice film by a constant flow of He-HCl after which a flow of HOCl-saturated He was added to the flow tube.

The concentration of HCl was always larger than that for $ClONO_2$ such that pseudo-first-order conditions prevailed. p_{HOCl} ranged from 1.3×10^{-7} to 1.8×10^{-6} Torr and p_{HCl} from 9×10^{-7} to 8×10^{-6} Torr. The observation of the HOCl decay led to an average uptake coefficient of 0.30±0.18, and the monitoring of the growth of Cl_2 led to a value for γ_{ss} of 0.38±0.24, the median of which is given in the Table. The results were independent of p_{HOCl}, p_{HCl}, and temperature within experimental variability, and all were corrected for gas-phase diffusion. This correction amounted to a factor exceding ten in some cases. Taking into account a structural model for the ice substrate, a value of $\gamma_{ss}=0.13\pm0.08$ was obtained which is approximately a factor of 2.6 smaller than the value based on the geometrical (external) surface. The surface roughness rather than the porosity of the film is seen as the principal parameter being responsible for the reduction of the measured γ_{ss}. The Cl_2 yield based on HOCl reacted was measured as 0.80±0.20.

Preferred Values

The uptake coefficient for HOCl in the presence of an excess of HCl on 60% *liquid* sulfuric acid was found to vary between 0.02 and 0.2 with temperature in the range 200–220 K. The uptake of HOCl is rate limiting in view of the faster uptake of HCl by approximately a factor of 6.

On NAT-like or water-rich substrates γ has been measured to be approximately 0.2 at 200 K. This value decreases by two orders of magnitude for conditions of low rh or correspondingly for HNO_3-rich NAT substrates.

Values of $\gamma=0.3$ are observed on water ice substrates at 190 K.

References

[1] D. R. Hanson and A. R. Ravishankara, J. Geophys. Res. **96**, 17307 (1991).
[2] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **96**, 2682 (1992).
[3] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **97**, 12309 (1993).
[4] J. P. D. Abbatt and M. J. Molina, Geophys. Res. Lett. **19**, 461 (1992).
[5] L. T. Chu, M.-T. Leu, and L. F. Keyser, J. Phys. Chem. **97**, 12798 (1993).

$BrONO_2 + H_2O \rightarrow HOBr + HNO_3$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\geqslant3.0\times10^{-1}$	H_2O-ice	200	Hanson and Ravishankara, 1993[1]	(a)

Comments

(a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS. Both the loss of $BrONO_2$ as well as the generation of HOBr were monitored. The uptake coefficient based on the loss of $BrONO_2$ and that based on the generation of the product HOBr were identical within the experimental uncertainty.

References

[1] D. R. Hanson and A. R. Ravishankara, NATO ASI Series (17), 281, in *The Tropospheric Chemistry of Ozone in the Polar Regions*, edited by H. Niki and K. H. Becker (Springer-Verlag, Berlin, 1993).

$BrONO_2 + HCl \rightarrow BrCl + HNO_3$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\sim 2.5\times10^{-1}$	H_2O-ice	200	Hanson and Ravishankara, 1993[1]	(a)

Comments

(a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS. Both the decrease in $BrONO_2$ and HCl as well as the formation of the products BrCl and HOBr were detected. There was, however, a monotonous decrease of HOBr with increasing injector distance which points to a competitive reaction between hydrolysis and halogen metathesis (title reaction). Analogous to the reaction $ClONO_2$ + HCl, the efficient secondary reaction between HOBr generated from the hydrolysis of $BrONO_2$ and HCl results in BrCl + H_2O.

References

[1] D. R. Hanson and A. R. Ravishankara, NATO ASI Series (17), 281, in *The Tropospheric Chemistry of Ozone in the Polar Regions*, edited by H. Niki and K. H. Becker (Springer-Verlag, Berlin, 1993).

$HBr + Cl_2 \rightarrow HCl + BrCl$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	3.0×10^{-1}	cold Pyrex at 50% rh	221	Hanson and Ravishankara, 1992[1]	(a)
	$\sim2.0\times10^{-1}$	H_2O-ice	221		

Comments

(a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS with selective detection of HBr and other halogen containing reactants and products. Ice layers 2–10 μm thick were condensed from the vapor phase onto the cold flow tube wall and HNO_3-treated ice was defined as NAT under the used experimental conditions. On cold Pyrex at 50% rh the stoichiometry of the reaction was observed as $2HBr + Cl_2 \rightarrow Br_2 + 2HCl$ because the quantity of HCl produced was equal to the amount of HBr and to twice the amount of Cl_2 lost. The reaction most likely proceeds through formation of BrCl that is consumed in a fast secondary reaction by excess HBr. On pure ice efficient loss of HBr and Cl_2 was observed where the loss of HBr was due to uptake by the ice substrate as well as due to the title reaction. In the absence of HBr a reactive uptake coefficient for loss of Cl_2 of $\leq 7 \times 10^{-4}$ was measured.

References

[1] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **96**, 9441 (1992).

$HOBr + HBr \rightarrow Br_2 + H_2O$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$(1.2\pm0.3)\times10^{-1}$	ice film	228	Abbatt, 1994[1]	(a)

Comments

(a) Flow tube study at a total pressure of 1 Torr He using a moveable injector and quadrupole MS sampling (HOBr at m/e 96, 98) at a slight excess of HBr. The HOBr was generated *in situ* inside a moveable injector tube by reaction of Br_2 with OH that was produced from NO_2 + H from a microwave discharge of H_2 in He. The ice film was prepared by wetting the flow tube wall and rapidly cooling to 228 K. The characteristic concentrations were $[HBr]\sim(6-15)\times10^{12}$ molecule cm^{-3}, $[HOBr]\sim(25)\times10^{12}$ molecule cm^{-3} and the uptake coefficient was measured by observation of the HOBr disappearance with injector position.

References

[1] J. P. D. Abbatt, Geophys. Res. Lett. **21**, 665 (1994).

$HOBr + HCl \rightarrow BrCl + H_2O$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$0.25^{+0.10}_{-0.05}$	ice film	228	Abbatt, 1994[1]	(a)

Comments

(a) Flow tube study at a total pressure of 1 Torr He using a moveable injector and quadrupole MS sampling (HOBr at m/e 96, 98) at a slight excess of HCl. The HOBr was generated *in situ* inside a moveable injector tube by reaction of Br_2 with OH that was produced from NO_2 + H from a microwave discharge of H_2 in He. The ice film was prepared by wetting the flow tube wall and rapidly cooling to 228 K. The characteristic concentrations were $[HCl]\sim(1-2)\times10^{12}$ molecule cm^{-3} (about a factor of four lower than the vapor pressure at which melting of the ice phase was previously observed) and $[HOBr]\sim10^{12}$ molecule cm^{-3}. An uptake coefficient of $0.3^{+0.7}_{-0.1}$ was measured by observing the increase of the product BrCl, consistent with the above measurement made by the observation of the HOBr disappearance.

References

[1] J. P. D. Abbatt, Geophys. Res. Lett. **21**, 665 (1994).

O_3 + Substrate (C_{am}) → products (O_2, CO, CO_2, {C_{am} O})

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_0	$(3.2\pm1.0)\times10^{-3}$	amorphous carbon	300	Stephens, Rossi, and Golden, 1986[1]	(a)
γ_{ss}	$(4.8\pm1.2)\times10^{-5}$ at $[O_3]=4.7\times10^{13}$ molecule cm^{-3}		300		
γ_{ss}	$>2.2\times10^{-3}$	carbon aerosol	300	Fendel and Schmidt Ott, 1993[2]	(b)

Comments

(a) Low pressure reactor study (Knudsen cell) with modulated molecular-beam sampling electron-impact MS detection. The solid substrate was bulk commercial-grade charcoal (Norit) of varying quantities (10–50 mg). Rapid poisoning of the surface took place with concomitant saturation of the uptake kinetics, usually within a few minutes. The decrease of the uptake coefficient in going from the initial to steady state uptake varied from a factor of eight at $[O_3]=2.8\times10^{14}$ molecule cm^{-3} to a factor of sixty at $[O_3]=3.2\times10^{13}$ molecule cm^{-3}. The rate law was not first order and could be represented by a fractional reaction order of $m = 0.633$ on the average. The sample could be restored close to its original state as measured by its uptake coefficient by heating in vacuum: CO_2, CO, and H_2O were observed as desorption products. The mass balance resulted in a CO_2/CO ratio of 2.5–4.0, depending on the O_3 density. For every molecule of O_3 adsorbed, one molecule of O_2 was detected. Between 12% and 23% of the adsorbed O_3 turned up as volatile carbon (CO_2, CO). With respect to odd oxygen, 20% to 35% left the carbon surface as CO_2 and CO with the balance staying on the carbon as some unidentified surface oxide.

(b) Flowing gas experiment of carbon aerosol in air exposed to ozone monitored using an electrochemical analyzer. The spark generator produced soot-like material of 10–100 nm radius, corresponding to agglomerates of fractal structure. The dimension of the carbon particulates corresponds to mobility-equivalent geometrical parameters. The collision cross sections derived from these mobility-equivalent parameters are thought to correspond to the gas kinetic collision cross section. Typically, an initial ozone concentration of 4×10^{12} molecule cm^{-3} decayed to 50% in the presence of 2.5 ng cm^{-3} of carbon aerosol after a reaction time of 30 s. Assuming an average diameter of 100 nm, one obtains a lower limit for the uptake coefficient of 2.2×10^{-3}.

References

[1] S. Stephens, M. J. Rossi, and D. M. Golden, Int. J. Chem. Kinet. **18**, 1133 (1986).

[2] W. Fendel and A. Schmidt Ott, J. Aerosol. Sci. **24**, Suppl. 1, S317 (1993).

$SO_2 + H_2O_2 \rightarrow H_2SO_4$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$(8.0\pm2.0)\times10^{3}$	pH=0.25, 1M H_2O_2 droplets	283	Jayne *et al.*, 1990[1]	(a)
	$(2.0\pm0.6)\times10^{-2}$	pH=2.0, 1M H_2O_2 droplets	283		
	$(3.5\pm0.4)\times10^{-2}$	pH=4.0, 1M H_2O_2 droplets	283		

Comments

(a) Uptake experiment on a fast moving droplet train traversing a flow tube coupled to tunable diode laser absorption of SO_2 in a multiple pass absorption cell (728 cm optical path). The measurement consists of monitoring the gas density in the flow tube with the droplet train switched on and off. The droplet size was 120 μm and the interaction time of the droplets with SO_2 was 2 and 10 ms. The SO_2 density was 4×10^{12} molecule cm^{-3} at a total pressure of 10 Torr (He + H_2O). A small admixture of CH_4 was used to control the degree of water saturation (=100%) of the carrier gas in order to prevent evaporation/condensation of the water droplets. The listed value has been corrected for gas-phase diffusion of SO_2 towards the droplet surface. The measured uptake coefficient is a composite of liquid diffusion limited uptake of S(IV), chemical reaction depending on the pH and saturation of the diffusion thickness layer (Henry's law saturation). These competing processes are all strongly pH dependent and lead to a complex pH dependence of γ. The presence of H_2O_2 induces significant uptake of SO_2 into the aqueous phase in the pH range 0–2 compared to the situation in the absence of H_2O_2 where reevaporation of SO_2 is dominant. The results are consistent with a maximum uptake coefficient of 0.11 which is a hypothetical value obtained in the absence of any surface saturation, diffusion, and chemical reaction rate limitation.

References

[1] J. T. Jayne, J. A. Gardner, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, J. Geophys. Res. **95**, 20559 (1990).

$COF_2 + H_2O \rightarrow 2HF + CO_2$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\leqslant 3\times10^{-6}$	ice, HNO_3-treated ice	192	Hanson and Ravishankara, 1991[1]	(a)
	$3.0^{+2}_{-3}\times10^{-6}$	60% H_2SO_4	215–230		
	6.0×10^{-5}	40% H_2SO_4	215–230		
γ	$<5\times10^{-4}$	water droplets, pH=1–14	275	De Bruyn *et al.*, 1992[2]	(b)
γ_{obs}	$(8\pm4)\times10^{-3}$	water droplets, pH=6	273	George *et al.*, 1994[3]	(c)

Comments

(a) Uptake experiment of COF_2 gas onto the walls of a coated flow tube. The kinetics were measured using a chemical ionization MS, observing CF_3O^- after reaction of CF_2O with SF_6^- or F^-. Typical densities of COF_2 used in the present study were between 10^{12} and 10^{13} molecule cm^{-3}. The ice and simulated NAT surfaces were stationary solid coatings at 192 K, whereas the 40% and 60% sulfuric acid flowed down the vertically mounted flow tube at T=215–230 K. On ice and simulated NAT surfaces no COF_2 uptake was observed, and the value given in the Table corresponds to an upper limit. Owing to the high densities of COF_2, experiments were performed to check the saturation behavior of COF_2. None was observed. It is thought that the uptake on 40% H_2SO_4 is due to chemical reaction rather than physical condensation.

(b) Uptake experiment on a fast monodisperse droplet train moving coaxially down a low pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase-sensitive detection. The total pressure was 6–20 Torr He, the droplet diameter was 50–200 μm, and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H_2O to result in a droplet temperature of 275 K. No uptake was detected for the droplet pH in the range 1–14 so that the value given in the Table represents an upper limit to the uptake coefficient.

(c) Uptake experiment of COF_2 gas in a reduced pressure flow tube in the presence of a fast moving monodisperse droplet train originating from a vibrating orifice. The pressure inside the flow tube was 20–25 Torr N_2, the diameter of the droplets lied between 100–110 μm, the droplet pH was varied between 3 and 10, and the contact times between 4 and 16 ms. The uptake kinetics were monitored using HPLC detection of the halogenide using conductometric (F^-) and UV detection (CF_3COOH). The temperature of the droplets was controlled by the H_2O vapor pressure in the flow tube and corresponded to T=273–294 K. Using the weak time- and temperature-dependence of γ_{obs} one obtains a Henry's law solubility of 35 and 22 mol dm^{-3} atm^{-1} and a hydrolysis rate constant of <1 and 30 s^{-1} at T=273 and 294 K, respectively. No pH dependence was detected.

References

[1] D. R. Hanson and A. R. Ravishankara, Geophys. Res. Lett. **18**, 1699 (1991).
[2] W. J. De Bruyn, S. X. Duan, X. Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, Geophys. Res. Lett. **19**, 1939 (1992).
[3] C. George, J. Y. Saison, J. L. Ponche, and P. Mirabel, J. Phys. Chem. **98**, 10857 (1994).

$COCl_2 + H_2O \rightarrow 2HCl + CO_2$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$<5\times10^{-4}$	water droplets, pH=1–14	275	De Bruyn *et al.*, 1992[1]	(a)

Comments

(a) Uptake experiment on a fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase sensitive detection. The total pressure was 6–20 Torr He, the droplet diameter was 50–200 μm, and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H_2O to result in a droplet temperature of 275 K. No uptake was detected for the droplet pH in the range 1–14 so that the value given in the Table represents an upper limit to the uptake coefficient.

References

[1] W. J. De Bruyn, S. X. Duan, X. Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, Geophys. Res. Lett. **19**, 1939 (1992).

$CCl_3COCl + H_2O \rightarrow CCl_3COOH + HCl$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	4.0×10^{-5} to 8.0×10^{-3}	water droplets, pH=6	275	De Bruyn *et al.*, 1992[1]	(a)
γ_{obs}	$(8\pm3)\times10^{-4}$	water droplets, pH=3.4	272–294	George *et al.*, 1994[2]	(b)

Comments

(a) Uptake experiment on fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase sensitive detection. The total pressure was 6–20 Torr He, the droplet diameter was 50–200 μm, and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H_2O to result in a droplet temperature of 275 K. Reactivity limited uptake of the title compound was observed at pH =13 and 14. The values given in the Table are obtained by extrapolation to pH=6. The lower limit is obtained by assuming the hydrolysis rate constant $k_{hyd} = k_p [OH^-]$ with $k_p = 1.6\times10^4$ dm^3 mol^{-1} s^{-1} from phosgene hydrolysis, whereas the upper limit results from direct scaling of the rate of phosgene hydrolysis at pH=6. The upper limit is preferred.

(b) Uptake experiment of CCl_3COCl gas in a reduced pressure flow tube in the presence of a fast moving monodisperse droplet train originating from a vibrating orifice. The pressure inside the flow tube was 20–25 Torr N_2, the diameter of the droplets between 100 and 110 μm, and the contact times between 4 and 16 ms. The temperature of the droplets was controlled by the H_2O vapor pressure in the flow tube and corresponded to T=274–294 K. The uptake was monitored by measuring the concentration of Cl^- in the droplets after collection and HPLC analysis. The uptake process of CCl_3COCl is complex and can be reduced to two competing steps of comparable rate: diffusion/uptake of the gas onto the surface and bulk of the droplet (Henry's law constant H) and hydrolysis (k_h). The observed uptake coefficient (see Table) was weakly dependent on the contact time and independent of pH in the range 3–12. This together with an estimated diffusion coefficient for CCl_3COCl in aqueous solution resulted in H =2.0 mol dm^{-3} atm^{-1} and k_h=500 s^{-1} for T=274 K with an uncertainty of a factor of two to three. The first-order rate constant k_h was also measured using the stopped flow technique in a dioxane-water solvent mixture and resulted in a value of 150±25 s^{-1} after extrapolation to pure water. The reaction was found to be acid and base catalyzed and k_h depended strongly on the presence of dioxane in the range 9.1–75% v. It also depended on the temperature and the presence of the acetate buffer.

References

[1] W. J. De Bruyn, S. X. Duan, X. Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, Geophys. Res. Lett. **19**, 1939 (1992).

[2] C. George, J. Lagrange, P. Lagrange, P. Mirabel, C. Pallares, and J. L. Ponche, J. Geophys. Res. **99**, 1255 (1994).

$CF_3COF + H_2O \rightarrow CF_3COOH + HF$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	1.2×10^{-6} to 2.4×10^{-4}	water droplets, pH=6	275	De Bruyn *et al.*, 1992[1]	(a)
γ_{obs}	$(7\pm2)\times10^{-4}$	water droplets, pH=6	274	George *et al.*, 1994[2]	(b)

Comments

(a) Uptake experiment on fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase-sensitive detection. The total pressure was 6–20 Torr He, the droplet diameter was 50–200 μm and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H_2O to result in a droplet temperature of 275 K. Reactivity-limited uptake of the title compound was observed at pH=13 and 14. The values given in the Table are obtained by extrapolation to pH=6. The lower limit is obtained by assuming the hydrolysis rate constant $k_{hyd} = k_p [OH^-]$ with $k_p = 1.6\times10^4$ l mol^{-1} s^{-1} from phosgene hydrolysis, whereas the upper limit results from direct scaling of the rate of phosgene hydrolysis at pH=6. The upper limit is preferred.

(b) Uptake experiment of CF_3COF gas in a reduced pressure-flow tube in the presence of a fast moving monodisperse droplet train originating from a vibrating orifice. The pressure inside the flow tube was 20–25 Torr N_2, the diameter of the droplets was between 100–110 μm, the droplet pH was varied between 3 and 10 and the contact times between 4 and 16 ms. The uptake kinetics were monitored using HPLC detection of the halogenide using conductometric (F^-) and UV detection (CF_3COOH). The temperature of the droplets was controlled by the H_2O vapor pressure in the flow tube and corresponded to T=273–294 K. Using the weak time- and temperature-dependence of γ_{obs}, one obtains a Henry's law solubility of 3 and 2.6 mol dm^{-3} atm^{-1} and a hydrolysis rate constant of 150 and 330 s^{-1} at T=273 and 294 K, respectively. No pH dependence was detected.

References

[1] W. J. De Bruyn, S. X. Duan, X. Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, Geophys. Res. Lett. **19**, 1939 (1992).

[2] C. George, J. Y. Saison, J. L. Ponche, and P. Mirabel, J. Phys. Chem. **98**, 10857 (1994).

$CF_3COCl + H_2O \rightarrow CF_3COOH + HCl$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	3.0×10^{-5} to 6.0×10^{-3}	water droplets, pH=6	275	De Bruyn *et al.*, 1992[1]	(a)
γ_{obs}	$(7\pm3)\times10^{-4}$	water droplets, pH=6	274	George *et al.*, 1994[2]	(b)

Comments

(a) Uptake experiment on fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase sensitive detection. The total pressure was 6–20 Torr He, the droplet diameter was 50–200 μm, and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H_2O to result in a droplet temperature of 275 K. Reactivity limited uptake of the title compound was observed at pH =13 and 14. The values given in the Table are obtained by extrapolation to pH=6. The lower limit is obtained by assuming the hydrolysis rate constant $k_{hyd}=k_p[OH^-]$ with $k_p=1.6\times10^4$ dm^3 mol^{-1} s^{-1} from phosgene hydrolysis, whereas the upper limit results from direct scaling of the rate of phosgene hydrolysis at pH=6. The upper limit is preferred.

(b) Uptake experiment of CF_3COCl gas in a reduced pressure flow tube in the presence of a fast moving monodisperse droplet train originating from a vibrating orifice. The pressure inside the flow tube was 20–25 Torr N_2, the diameter of the droplets was between 100–110 μm, the droplet pH was varied between 3 and 10, and the contact times between 4 and 16 ms. The uptake kinetics were monitored using HPLC detection of the halogenide using conductometric (Cl^-) and UV detection (CF_3COOH). The temperature of the droplets was controlled by the H_2O vapor pressure in the flow tube and corresponded to T=273–294 K. No pH or temperature dependence of γ_{obs} was detected. Using the weak time and temperature dependence of γ_{obs} one obtains a Henry's law solubility of 4 mol $dm^{-3}atm^{-1}$ and a hydrolysis rate constant of 50 s^{-1} at T=273 K.

References

[1] W. J. De Bruyn, S. X. Duan, X. Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, Geophys. Res. Lett. **19**, 1939 (1992).

[2] C. George, J. Y. Saison, J. L. Ponche, and P. Mirabel, J. Phys. Chem. **98**, 10857 (1994).

NO_2/N_2O_4 + Substrate (amorphous Carbon, NaCl) → products

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_0	$(6.4\pm2.0)\times10^{-2}$	amorphous carbon	300	Tabor, Gutzwiller, and Rossi, 1993[1], 1994[2]	(a)
γ_3	$(6.0\pm2.0)\times10^{-5}$	N_2O_4 + NaCl, dry	300	Vogt and Finlayson-Pitts, 1994[3]	(b)

Comments

(a) Uptake experiment in a low-pressure reactor (Knudsen cell) monitored by modulated molecular beam sampling electron-impact MS and *in situ* laser-induced fluorescence. In addition to steady-state uptake experiments of NO_2 on three different samples of amorphous carbon, each characterized by its BET surface area (20, 115, and 460 m^2 g^{-1}), pulsed valve experiments limited the NO_2 dose to the solid carbon sample and resulted in real-time measurements of the NO_2 lifetime in the presence of the carbon surface. The initial adsorption kinetics were identical for all three amorphous carbon samples within the experimental uncertainty, indicating that the uptake is independent of the microscopic details of the surface. Chemical kinetic modeling was used to explain the pulsed as well as the steady-state uptake curves obtained over a range of two orders of magnitude in NO_2 flow rates (2×10^{14} to 2

$\times 10^{16}$ molecule s^{-1}) and a factor of 15 in residence time. The reaction mechanism was complex and included surface saturation as well as competitive adsorption to nonreactive adsorption sites leading to inhibition effects at higher pressures. The pressure in the Knudsen cell was sufficiently low to exclude the participation of N_2O_4 in the uptake. NO was the only major product and was formed in decreasing yields with decreasing BET surface area, starting at 100%. Repetitively exposed carbon samples were subject to severe poisoning effects that were partially reversible upon prolonged pumping or heat treatment under vacuum.

(b) The reaction resulted in the formation of NOCl and solid $NaNO_3$ and was followed by monitoring the formation of nitrate on the surface of the ground NaCl sample as a function of time using diffuse reflectance FTIR. The rate of nitrate formation was obtained from the integrated area of all absorptions in the region of the antisymmetric NO_3^- stretch (1390 cm^{-1} band). The cell residence time was on the order of 3 s, the NO_2 concentration was in the range $(1.8-29)\times 10^{14}$ molecule cm^{-3} at 30 mbar total pressure, and the extent of reaction was kept small. The rate law was obtained and resulted in a second-order dependence of the rate of nitrate formation on NO_2 concentration. The heterogeneous reaction was interpreted using a mechanism wherein N_2O_4 directly reacted with NaCl resulting in NOCl (not observed) and $NaNO_3$. The γ value listed in the Table therefore refers to the uptake of N_2O_4 in equilibrium with NO_2, as the dimer seems to be the active species under the given pressure and temperature conditions of the uptake experiment. Complicating factors found in the course of the diffuse reflectance FTIR spectroscopic study were uncertainties regarding the penetration depth of the IR radiation, nitrate concentration gradients, and H_2O adsorption. Two different kinds of adsorbed nitrate were observed and the interconversion between the two forms was facilitated by adsorbed H_2O forming a quasi-liquid layer.

References

[1] K. Tabor, L. Gutzwiller, and M. J. Rossi, Geophys. Res. Lett. **20**, 1431 (1993).

[2] K. Tabor, L. Gutzwiller, and M. J. Rossi, J. Phys. Chem. **98**, 6172 (1994).

[3] R. Vogt and B. J. Finlayson-Pitts, J. Phys. Chem. **98**, 3747 (1994).

5.2.2. Uptake Kinetics without Chemical Reaction

HO_2 + Substrate (SiO_2, H_2O-Aerosol)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_0	$(5.3\pm4.5)\times 10^{-1}$	r=0.055 mm NH_4HSO_4	300	Mozurkewich *et al.*, 1987[3]	(a)
	$(3.4\pm1.0)\times 10^{-1}$	r=0.081 mm NH_4HSO_4	300		
γ_{ss}	$(1-3)\times 10^{-3}$	SiO_2	300–369	Antsupov, Ksandopulo, and Gershenzon, 1990[2]	(b)
γ_{ss}	$>1.0\times 10^{-2}$	fluid film	275	Hanson *et al.*, 1992[3]	(c)
	$>5.0\times 10^{-2}$	28% H_2SO_4	249		

Comments

(a) Atmospheric pressure flow tube experiment with chemical detection of HO_2 using a fast chain chemical amplification of HO_2 coupled to NO_2 chemiluminescence detection. The HO_2 was generated by thermal dissociation of H_2-H_2O over a hot NiCr wire with estimated HO_2 densities of 10^8 to 10^9 molecule cm^{-3}. The aerosol was produced from atomizing salt solutions and size selected by a Differential Mobility Analyzer. The fraction selected was monodisperse (particle radii within ±14%) and contained typically $(2-3)\times 10^5$ particles cm^{-3}. A Cu(II) salt was added to the solution in order to oxidize HO_2 to H_2O_2 in solution thus preventing reevaporation of HO_2. The uptake efficiency has therefore to be interpreted as the kinetics of HO_2 accommodation on the surface of fine aqueous aerosol particles. The pseudo-first-order rate coefficient for loss of HO_2, k_I, was interpreted in terms of HO_2 wall loss (k_w) and a second-order rate coefficient (k_{II}) for the loss of HO_2 on the surface of the aerosol: $k_I = k_w + k_{II} N$ (N=number of particles). The authors conclude that the Cu(II) concentration used in their experiments (up to 0.0063 mole kg^{-1} solution) may have been only marginally sufficient to trap the HO_2. The uptake coefficient of HO_2 on $LiNO_3$ aerosol (r=0.054 μm) was 0.57 ± 0.16.

(b) Flowing gas experiment in an all-quartz flow tube reactor using a microwave sustained cool flame of 100:1 oxygen and ethanol or allyl alcohol at pressures of 5.3–12.8 Torr. HO_2 was detected by LMR and γ was found to be independent of the total pressure in the range 5.3–12.8 Torr. At higher pressure the homogeneous disproportionation reaction becomes increasingly important. It was observed that γ has a strong negative temperature dependence, which was interpreted in terms of increasing passivation of the quartz surface by alcohol combustion products. However, reference experiments with added H_2O led to a decrease in γ, reportedly because of blocking of active surface sites for adsorption of HO_2 on quartz. The specific-temperature dependent values of γ were $\gamma=1.5\times10^{-5}\exp[(1430\pm50)/T]$ for ethanol and $\gamma=1.6\times10^{-5}\exp[(1540\pm120)/T]$ for allyl alcohol.

(c) Uptake experiment in a wetted-wall flow tube reactor. The HO_2 free radical was generated through the reaction F + $H_2O_2 \rightarrow HO_2$ + HF using a microwave discharge. The HO_2 density was measured by titration with NO, and the resulting OH was monitored using pulsed LIF excited at 282 nm and detected at 308±4 nm. The HO_2 density was between $(0.5-3)\times10^{11}$ molecule cm^{-3} and no homogeneous self-reaction was expected. Deionized water was flowing down the vertical flow tube at 274.5 K in one series of experiments (9 Torr total pressure), and a fluid 28% H_2SO_4-H_2O mixture in another series of experiments at 249.5 K (1.6 Torr total pressure). Precautions were taken to achieve complete saturation of the He flow with H_2O, and the analysis included full treatment of gas-phase (radial) diffusion. The measured first-order rate coefficients for the HO_2 reaction on the fluid H_2O film were extrapolated to zero carrier flow speed in order to approach the limit of vanishing Reynolds number. The listed γ values for both the fluid water film and the aqueous H_2SO_4 experiment are very sensitive to uncertainties in the diffusion coefficient and the measured k_w because the kinetics is close to the diffusion limit. Therefore only lower limits for γ are given.

References

[1] M. Mozurkewich, P. H. McMurry, A. Gupta, and J. G. Calvert, J. Geophys. Res. **92**, 4163 (1987).

[2] E. V. Antsupov, G. I. Ksandopulo, and Yu. M. Gershenzon, Sov. J. Chem. Phys. **6**, 2500 (1990).

[3] D. R. Hanson, J. B. Burkholder, C. J. Howard, and A. R. Ravishankara, J. Phys. Chem. **96**, 4979 (1992).

OH + Substrate (H_2O, SiO_2, H_2SO_4)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$(10.0\pm3.0)\times10^{-3}$	acid-washed SiO_2	300	Gershenzon *et al.*, 1985[1]	(a)
	$(5.0\pm2.0)\times10^{-3}$	HF-etched SiO_2	300		
	$\geqslant4.0\times10^{-1}$	H_2O-ice	253		
	$\leqslant1.0$	96% H_2SO_4	298		
γ_{ss}	3.5×10^{-3}	fluid H_2O film	275	Hanson *et al.*, 1992[2]	(b)
	$>8.0\times10^{-2}$	28% H_2SO_4	249		

Comments

(a) Flowing gas experiment in an all-quartz flow tube reactor coupled to a combined EPR/LMR detector for OH radicals at pressures in the range 1–4.5 Torr and residence times up to 200 ms. The all-quartz flow tube reactor was coated either with fluorinated Teflon or with the material of interest (96% H_2SO_4, water-ice) and was equipped with a jacket for circulation of a temperature controlled fluid used in the temperature range 253–348 K. The OH radical was generated from the reaction H + $NO_2 \rightarrow$ OH + NO using a microwave discharge of a 0.1% H_2-He mixture. Typical densities were $[H]=(1-3)\times10^{13}$ molecule cm^{-3}, $[NO_2]=(1-2)\times10^{12}$ molecule cm^{-3} and $[OH]\leqslant2\times10^{12}$ molecule cm^{-3}. At those densities no homogeneous OH self-reactions were important, and no correction for diffusive transport was deemed necessary. For the Teflon surface a strong negative temperature dependence was noted: $\gamma=3.9\times10^{-6}\exp[(1610\pm554)/T]$, and there was a significant difference in γ for single and double Teflon-coatings (the expression applies to a triply Teflon coated surface). In contrast, CrO_3-treated quartz surfaces showed a positive temperature dependence with $\gamma=8.3\times10^{-2}\exp[(-654\pm151)/T]$, whereas results for a HF-treated quartz surface did not show a significant temperature dependence. The γ value for ice (253 K) was measured at 1.5 Torr of He, and that for 96% H_2SO_4 at 4.5 Torr.

(b) Uptake experiment in a wetted-wall flow tube reactor. The OH free radical was generated through the reaction H + $NO_2 \rightarrow$ OH + NO under conditions of excess H, and OH radicals were monitored using pulsed LIF excited at 282 nm and detection at 308 ± 4 nm. The OH radical density was between $(0.5-3)\times10^{11}$ molecule cm^{-3} at H atom densities of $10^{11}-10^{12}$ molecule cm^{-3}. Deionized water was flowing down the vertical flow tube at 274.5 K in one series of experiments (9 Torr total pressure), and a fluid 28% H_2SO_4-H_2O mixture in another series of experiments at 249.5 K (1.6 Torr total pressure). Precautions were taken to achieve complete saturation of the He flow with H_2O, and the analysis included full treatment of gas-phase (radial) diffusion. The measured first-order rate constants for the OH radical reaction on the fluid H_2O film were extrapolated to zero carrier flow speed in order to approach the limit of vanishing Reynolds number. The listed γ value for the aqueous H_2SO_4 experiment is very sensitive to uncertainties in the diffusion coefficient and the measured k_w because the kinetics is close to the diffusion limit. Therefore only lower limits for γ are given.

References

[1] Y. M. Gershenzon, A. V. Ivanov, S. I. Kucheryavyi, and V. B. Rozenshtein, Kinetika i Kataliz, **27**, 1069 (1986).

[2] D. R. Hanson, J. B. Burkholder, C. J. Howard, and A. R. Ravishankara, J. Phys. Chem. **96**, 4979 (1992).

H_2O + Substrate (water ice, NAT, NaCl)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$0.3^{+0.7}_{-0.1}$	ice film	195	Leu, 1988[1]	(a)
γ_{ss}	1.06 ± 0.10	ice film	20	Haynes, Tro, and George, 1992[2]	(b)
	$(6.5\pm0.8)\times10^{-1}$	ice film	185		
γ_{ss}	$2.0\times10^{-3}\leq\gamma\leq1.0\times10^{-2}$	NAT	197	Middlebrook *et al.*, 1992[3]	(c)
γ_{ss}	$<2.0\times10^{-4}$	dry NaCl, rh≤1%	300	Fenter, Caloz, and Rossi, 1994[4]	(d)

Comments

(a) Fast flow tube reactor with electron-impact MS sampling as a diagnostic. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total). Owing to the large value of γ a diffusion correction had to be applied to the uptake rate coefficient using the measured diffusion coefficient of H_2O in He scaled to 195 K.

(b) Ultra-high vacuum interferometric observation of the growth and evaporation of H_2O as a function of temperature. Three different types of experiments were performed: measurement of the thickness of the H_2O multilayer (sub μm) as a function of time at a given static pressure of H_2O, isothermal evaporation into the vacuum, and quasiequilibrium studies at constant temperature by setting the water vapor pressure to balance condensation and evaporation. The ''evaporation coefficient'' is numerically equal to the condensation coefficient in the temperature where it could be measured (175–205 K) and was found to have an activation energy of 49.8 ± 0.8 kJ mol^{-1} using a zero-order rate law appropriate for multilayer desorption. A precursor-mediated adsorption/desorption model was used to explain the negative temperature dependence of the condensation coefficient. A sublimation enthalpy of H_2O ice has been obtained from the quasiequilibrium measurement of the vapor pressure as a function of temperature. $\Delta H_{sub}=49.4\pm0.8$ kJ mol^{-1} and $\Delta S_{sub}=129.7$ J K^{-1} mol^{-1} have been obtained, in excellent agreement with the kinetic results of the activation energy for evaporation. Therefore, no barrier exists for adsorption and desorption of H_2O onto itself. No dependence of the kinetic parameters on the various ice modifications has been observed.

(c) Isothermal film growth experiment in a static chamber with time-dependent FTIR monitoring of optical density of depositing NAT film at 3371 cm^{-1} in absorption. Absolute calibration of the thickness of the NAT deposited film was performed by observing the optical interference (fringes) in the range 4000–7000 cm^{-1} assuming a refractive index of 1.45 for NAT. The pressures were chosen to simulate stratospheric conditions with $p(H_2O)=1.5\times10^{-4}$ Torr and $p_{HNO3}=(4-10)\times10^{-7}$ Torr. The spread of the γ values given in the Table corresponds to the range in the HNO_3 pressure. A doubling of the H_2O and the upper limit of the HNO_3 pressure left the uptake coefficient unchanged.

(d) Transient uptake experiment of H_2O on dry NaCl in a low-pressure reactor (Knudsen cell) with modulated molecular-beam sampling and phase sensitive detection using an electron-impact quadrupole MS. The H_2O was dosed onto the salt surface using a pulsed valve and gave rise to a transient H_2O pressure on the order of a mTorr. No significant uptake of H_2O vapor by NaCl could be observed.

References

[1] M.-T. Leu, Geophys. Res. Lett. **15**, 17 (1988).

[2] D. R. Haynes, N. J. Tro, and S. M. George, J. Phys. Chem. **96**, 8504 (1992).

[3] A. M. Middlebrook, B. G. Koehler, L. S. McNeill, and M. A. Tolbert, Geophys. Res. Lett. **19**, 2417 (1992).

[4] F. F. Fenter, F. Caloz, and M. J. Rossi, J. Phys. Chem. **98**, 9801 (1994).

HCl + Substrate (water ice, NAT, H_2SO_4/H_2O, NaCl)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
	Sulfate/H_2SO_4 (liquid) Substrates				
γ_{ss}	1.5×10^{-3}	65% H_2SO_4	210	Tolbert, Rossi, and Golden, 1988[1]	(a)
	2.6×10^{-4}	70% H_2SO_4	220		
	$\geqslant8.5\times10^{-5}$	75% H_2SO_4	230		
γ	$(1.5\pm0.3)\times10^{-1}$	0–40% H_2SO_4 droplet	300	Watson *et al.*, 1990[2]	(b)
	$(1.04\pm0.12)\times10^{-1}$	47% H_2SO_4 droplet	300		
	$(7.8\pm0.6)\times10^{-2}$	52% H_2SO_4 droplet	300		
	$(1.0\pm0.4)\times10^{-2}$	73% H_2SO_4 droplet	300		
γ_{ss}	$\geqslant5.0\times10^{-2}$	40% H_2SO_4	218 ± 3	Hanson and Ravishankara, 1991[3]	(c)
	4.0×10^{-4}	60% H_2SO_4	215		
	$<3.0\times10^{-5}$	65% H_2SO_4	215		
	$<1.0\times10^{-5}$	70% H_2SO_4	220		
	HNO_3-H_2O Substrates				
γ_{ss}	$\geqslant2.0\times10^{-1}$	NAT film	202	Abbatt and Molina, 1992[4]	(d)
γ_{ss}	$>2.0\times10^{-1}$	NAT film	188, 193	Chu, Leu, and Keyser, 1993[5]	(e)
	H_2O (solid) Substrates				
γ_{ss}	$0.4^{+0.6}_{-0.2}$	ice film	197	Leu, 1988[6]	(f)
γ_{ss}	$(4.0\pm2.0)\times10^{-2}$	ice film	196	Leu, Moore, and Keyser, 1991[7]	(g)
γ_{ss}	$\geqslant0.3^{+0.7}_{-0.1}$	ice film	190	Hanson and Ravishankara, 1992[8]	(h)
γ_{ss}	$>2.0\times10^{-1}$	H_2O-ice film	188, 193	Chu, Leu, and Keyser, 1993[5]	(e)
	H_2O (liquid) Substrates				
γ	$(6.4^{+1.2}_{-0.8})\times10^{-2}$	H_2O droplet	294	Van Doren *et al.*,1990[9]	(i)
	$(1.77\ ^{+0.24}_{-0.17})\times10^{-1}$	H_2O droplet	274		
γ	$2.0\times10^{-2}\geqslant\gamma\geqslant1.0\times10^{-2}$	liquid jet	296.7	Kirchner *et al.*, 1990[10]	(j)
	Other Substrates				
γ_0	3.0×10^{-3}	dry NaCl, rh$\leqslant$1%	300	Fenter, Caloz, and Rossi, 1994[11]	(k)

Comments

(a) Uptake experiment in a Knudsen cell flow reactor coupled to a molecular beam sampled electron-impact MS. The bulk substrate (1–5 mL) was cooled slowly to temperatures of 210–230 K. The H_2SO_4 concentration in the bulk was obtained by dilution from 96.5% H_2SO_4 and was chosen to reflect the sulfuric acid aerosol concentration under stratospheric conditions, that is in the temperature range 210–230 K. The measured steady-state H_2O vapor pressure in the Knudsen cell was 4×10^{-4} Torr ($\pm30\%$). The listed γ values in the Table were measured under steady-state conditions, and the value for 75% H_2SO_4 is thought to be a lower limit to the uptake efficiency owing to diffusion limitation of HCl in the sulfuric acid. Less than 5% of HCl was desorbed from a 65% H_2SO_4-H_2O solution at 253 K.

(b) Uptake experiment in a gas-droplet flow tube apparatus of transverse geometry coupled to a multiple path IR diode laser absorption cell of 728 cm optical path. The droplet diameter ranged from 110 to 280 mm and the interaction time of the sulfuric acid droplets with the HCl was varied from 2 to 0.7 ms. The HCl density was kept below 8×10^{12} molecule cm^{-3} and the total pressure (H_2O + He) ranged from 4 to 10 Torr. The γ values listed in the Table are corrected for gas-phase diffusion. Saturation phenomena became apparent at high acidities (pH$=-3$) and long interaction times.

(c) Uptake experiment in a wetted-wall flow tube with chemical ionization MS detection. This method allows selective detection of reactants at characteristic densities of 10^{10} to 10^{11} molecule cm^{-3}. The cold aqueous solution of H_2SO_4 (40 to 75% by weight, T=215 to 230 K) was flowing down the walls of the flow tube with a liquid film residence time of 20–30 s. $p(H_2O)$ was generally around 1 mTorr. In general, there is very little uptake of HCl on liquid aqueous solutions except for 40% H_2SO_4. The error limits were reported as $^{+100}_{-50}\%$.

(d) Uptake experiment in an ice-coated flow tube using electron-impact quadrupole MS equipped with a closed ion-source. Uptake study of HCl on NAT with careful control of the thermodynamic surface state of the cryogenic substrate with characteristic pressures of HCl of $\sim10^{-6}$ Torr. The NAT films were prepared starting from 10 μm thick ice films that were exposed to small pressures of HNO_3 over long periods of time resulting in a 0.1 μm thick NAT layer on top of the ice film. On HNO_3-rich NAT only small amounts of HCl were taken up, usually $<10^{13}$ molecule cm^{-2} except at high p_{HCl}. On H_2O-rich NAT the HCl reached monolayer coverage, 10^{15} molecule cm^{-2} (10 Å^2 cross-section) already at low p_{HCl} (5×10^{-6} Torr). There were two regimes for HCl adsorption separated by a threshhold pressure p_{HCl} depending on $p(H_2O)$ in an inverse manner: For $p(H_2O)=(2–5)\times10^{-4}$ Torr leading to

HNO_3-rich NAT, $p_{HCl}=10^{-4}$ Torr; for $p(H_2O)=10^{-3}$ Torr, $p_{HCl}=3\times10^{-5}$ Torr; for $p(H_2O)=1.5\times10^{-3}$ Torr leading to H_2O-rich NAT, $p_{HCl}=10^{-5}$ Torr. Below p_{HCl} the HCl adsorption was weak, reversible, and saturable. The adsorption of HCl at pressures greater than the corresponding threshhold value was unlimited in time and thus not saturable. It is thought that this situation corresponds to uptake of HCl by a molten liquid phase on the surface of the cryogenic substrate resulting in a H_2O-HNO_3-HCl solution at 202 K. The measured vapor pressure of H_2O corresponds to the one for pure ice at 202 K (1.7 mTorr) and is apparently controlled by the underlying solid ice phase. Sizable amounts of HCl can apparently be adsorbed only above a molten surface phase whose stability is given by the composition of the cryogenic phase (HNO_3-H_2O) and p_{HCl}.

(e) Uptake experiment performed in an ice- and HNO_3-doped ice-coated flow tube coupled to a differentially pumped electron-impact quadrupole MS in the ioncounting mode. Characteristic pressures of HCl and other reactants were of the order of 10^{-7} Torr. No explicit uptake kinetics are reported owing to the rapid uptake of HCl on both ice and HNO_3-doped ice. The cryogenic surfaces were deposited onto the cold walls of the flow tube from the vapors entrained in He from the corresponding liquids. The HNO_3 content was verified using acid-base titration. The mole fraction taken up by pure water ice was in the range 3.3×10^{-5} to 6.4×10^{-4} at p_{HCl} of 7×10^{-8} to 6×10^{-6} Torr in the temperature range 188–193 K. The amount taken up by ice increased with p_{HCl} and decreasing temperature. For an increase in ice thickness from 0.5 to 15.7 μm a factor of five increase of the HCl taken up by the ice was observed at $p_{HCl}=(2.1\pm0.1)\times10^{-7}$ Torr and $T=188$ K. The HCl uptake on HNO_3-doped ice ranged from $(2.8-24)\times10^{-6}$ mole fraction at $p_{HCl}=4.5\times10^{-5}$ Torr at 188 K and 1.6 μm substrate thickness. A fast HCl adsorption was followed by an isothermal desorption of HCl for a HNO_3-H_2O composition of 47.1%. Curiously, concomitantly with HCl desorption an increase of HNO_3 and a decrease of H_2O vapor pressure were observed perhaps indicating transient formation of NAD upon exposure of NAT to HCl.

(f) Uptake experiment performed in a fast flow tube reactor with electron-impact MS sampling. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total). Owing to the large value of γ a diffusion correction had to be applied to the uptake rate coefficient using estimated diffusion coefficients scaled to 197 K.

(g) Uptake experiment in an ice-coated flow tube using electron-impact MS with ion-counting. The substrates were prepared by bubbling He through a HNO_3-H_2O solution and subsequently condensing the mixture (NAT films) at 196 K resulting in film thicknesses of 70 μm. The surface areas and bulk densities of condensed films were measured *ex situ* in addition to the measurement of their FTIR absorption spectra. The reported data were corrected for external diffusion (important for large values of γ) using estimated diffusion coefficients in He as well as for pore diffusion (important for small values of γ) using a (semiquantitative) two-site surface reaction model: ice and NAT films were weighted according to their corresponding mass fractions. The characteristic pressures of HCl were in the mTorr range (± one decade) and γ given in the Table corresponds to the fitted parameters for the pure phases of ice and stoichiometric NAT even though only NAT samples of varying compositions were used (44.2 to 57.4% HNO_3 H_2O). The measured values for γ on samples of varying HNO_3-NAT composition, corrected for external diffusion, were in the range 0.01–10^{-6}. The authors note an "induction" period of several minutes during which the uptake coefficient increased up to a factor of five.

(h) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of reactants at characteristic densities of 10^9 to 10^{11} molecule cm^{-3}. At high values of the uptake coefficient ($\gamma\geqslant0.1$) significant diffusion corrections had to be made using calculated diffusion coefficients for the reactants in He. At low HCl concentrations (10^{10} molecule cm^{-3}) rapid saturation of the pure ice surface was observed within one minute and γ decreased from $\geqslant0.3$ to <0.01. The dose to saturation was essentially a monolayer or so: 5×10^{14} molecule cm^{-2} for pure ice, half that value for NAT. HCl is thought to remain adsorbed onto the surface: the diffusion into the bulk is extremely slow at 190 K. Only 50% of the HCl can be recovered. At high HCl concentrations (2×10^{12} molecule cm^{-3}) there was unlimited uptake at $\gamma>0.3$. At those high HCl densities either a stable hexahydrate ($HCl.6H_2O$) or a metastable supercooled liquid is formed. Whatever the new phase, the uptake coefficient is independent of the condensed phase and controlled by the steady-state pressure of water (2×10^{-4} Torr at 191 K).

(i) Uptake experiment on a fast droplet train (200 μm diameter) crossing a flow tube in transverse geometry. Trace gas analysis was by IR diode laser absorption in a multiple pass cell of 728 cm optical path at total pressures of 5–20 Torr. Values listed are corrected for gas-phase diffusion and distortion of velocity vector owing to rapid uptake.

(j) Uptake experiment involving the interaction of HCl in an atmospheric pressure of synthetic air with a liquid jet of pure water. The uptake kinetics were studied by analyzing the liquid water content for Cl^- using ion chromatography. The jet diameter was 90 μm, the jet length between 0.2 and 6 mm leading to contact times of 0.03–1.0 ms. The uptake coefficient was interpreted as a mass accommodation coefficient after fitting of the concentration of anions in the collected sample with the jet length taking into account the diffusion coefficients for the gas and liquid phase as well as the Henry's law constants. The results are regarded as lower limits owing to uncertainties in the velocity distribution of the liquid jet. The HCl concentration was about 223 ppm. The mass accommodation coefficient showed a weak dependence on the mean speed of the jet (10–750 cm s^{-1}) and was independent of the relative humidity (0–48%) of the gas phase.

(k) Uptake experiment involving HCl on dry NaCl in a low-pressure reactor (Knudsen cell) with modulated molecular-beam sampling and phase sensitive detection using an electron-impact quadrupole MS. The initial uptake at a flow of 5×10^{14} molecule s^{-1} depended only on the external (geometric) sample surface and was independent of the mass and grain size of the salt sample.

Preferred Values

The uptake coefficient of HCl on bulk substrates of *liquid* sulfuric acid at $T=220$ K is strongly anticorrelated with the H_2O activity of these mixtures and is comparable in magnitude and behavior with γ for $ClONO_2 + H_2O$ and $ClONO_2 + HCl$. It spans the range of γ values of 0.1 to 10^{-5}. The solubility of HCl in those mixtures seems to be the controlling factor. This drop in γ with decreasing H_2O activity is less pronounced for *droplets* interacting with HCl at 300 K. The uptake coefficient is 0.15 for 0 to 40% sulfuric acid at ambient temperature and is interpreted as accommodation coefficient. This behavior confirms a trend where the accommodation coefficient on droplets seems to be larger than the limiting uptake coefficient on the corresponding bulk phase after suitable correction for saturation and temperature.

On NAT-like substrates and on water ices γ has been found to be large, of the order of 0.2. On water ice γ has been found to be large, of the order of 0.3. On liquid water droplets the uptake coefficient is significantly smaller of the order of ≤ 0.1 at ambient temperature. On lowering the temperature by 20 K, γ increases to 0.2.

References

[1] M. A. Tolbert, M. J. Rossi, and D. M. Golden, Geophys. Res. Lett. **15**, 847 (1988).
[2] L. R. Watson, J. M. Van Doren, P. Davidovits, D. R. Worsnop, M. Zahniser, and C. E. Kolb, J. Geophys. Res. **95**, 5631 (1990).
[3] D. R. Hanson and A. R. Ravishankara, J. Geophys. Res. **96**, 17307 (1991).
[4] J. P. D. Abbatt and M. J. Molina, J. Phys. Chem. **96**, 7674 (1992).
[5] L. T. Chu, M.-T. Leu, and L. F. Keyser, J. Phys. Chem. **97**, 7779 (1993).
[6] M.-T. Leu, Geophys. Res. Lett. **15**, 17 (1988).
[7] M.-T. Leu, S. B. Moore, and L. F. Keyser, J. Phys. Chem. **95**, 7763 (1991).
[8] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **96**, 2682 (1992).
[9] J. M. Van Doren, L. R. Watson, P. Davidovits, D. R. Worsnop, M. Zahniser, and C. E. Kolb, J. Phys. Chem. **94**, 3265 (1990).
[10] W. Kirchner, F. Welter, A. Bongartz, J. Kames, S. Schweighoefer, and U. Schurath, J. Atm. Chem. **10**, 427 (1990).
[11] F. F. Fenter, F. Caloz, and M. J. Rossi, J. Phys. Chem. **98**, 9801 (1994).

HOCl + Substrate (water ice)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\geq(0.3^{+0.7}_{-0.1})$	ice film	191–211	Hanson and Ravishankara, 1992[1]	(a)
γ_{ss}	$\geq 3.0\times10^{-1}$	ice film	195–208	Abbatt and Molina, 1992[2]	(b)

Comments

(a) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of HOCl at characteristic densities of 10^9 to 10^{11} molecule cm^{-3}. At high values of the uptake coefficient ($\gamma\geq0.1$) significant diffusion corrections had to be made using calculated diffusion coefficients for the reactants in He. The primary observable was a first-order loss rate coefficient from which γ was calculated taking into account the diffusion correction and the corrected gas-wall collision frequency in the presence of a reactive surface. The source of HOCl was either from the reaction HCl + $Ca(ClO)_2$ or from the *in situ* reaction of $ClONO_2 + H_2O$ (ice). The thermodynamics of adsorption were measured from the integrated (relative) HOCl signal over the temperature range 191–211 K and resulted in the following values: $\Delta H_{ads}=-(58.6\pm8.4)$ kJ mol^{-1}, $\Delta S_{ads}=-(167.3 \pm41.8)$ J mol^{-1} K^{-1} (estimated). The fractional surface coverage in all the reported experiments did not exceed 0.01. HOCl does not adsorb on NAT nor is it formed from the reaction $ClONO_2 + H_2O$ on NAT under the given experimental conditions.

(b) Uptake experiment in an ice-coated flow tube using electron-impact quadrupole MS equipped with a closed ion-source. No specific value for the uptake kinetics was given. A surface coverage estimate yields 3.2×10^{13} molecule cm^{-2} at a HOCl pressure of 3×10^{-6} Torr, representing 5% of a monolayer on ice with 0.15 nm^2 of (estimated) cross-sectional area. The heat of adsorption was determined to be (43.9 ± 8.4) kJ mol^{-1}.

References

[1] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **96**, 2682 (1992).
[2] J. P. D. Abbatt and M. J. Molina, Geophys. Res. Lett. **19**, 461 (1992).

HBr + Substrate (water ice, NAT)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	0.3–1.0	water-ice, NAT	201	Hanson and Ravishankara, 1992[1]	(a)

Comments

(a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS with selective detection of HBr and other halogen containing reactants and products. Ice layers 2–10 μm thick were condensed from the vapor phase onto the cold flow tube wall and HNO_3-treated ice was defined as NAT under the used experimental conditions. The uptake of HBr on pure ice is very efficient with no signs of saturation up to 10 monolayers of HBr on ice (5×10^{15} molecule cm^{-2}) at HBr concentrations as low as 2×10^{10} molecule cm^{-3}. It is thought that a new fluid binary phase HBr-H_2O forms at HBr pressures as low as 6×10^{-9} Torr explaining the unlimited HBr uptake, rather than being due to a physical uptake process. No significant uptake of HBr on cold Pyrex was observed ($\gamma_{ss}=1.0\times10^{3}$), however, the uptake was significantly enhanced on HF-treated cold Pyrex reaching values up to 0.10. In contrast, significant uptake of HBr was observed when HBr was introduced into the tube concomitantly with H_2O vapor at 50% relative humidity at 201 K. Again, a binary fluid mixture HBr-H_2O is thought to form at HBr pressures $\geq5\times10^{-7}$ Torr.

References

[1] D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **96**, 9441 (1992).

HOBr + Substrate (Pyrex, water ice, H_2SO_4/H_2O)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$(2\text{-}4)\times10^{-4}$	Pyrex	228	Abbatt, 1994[1]	(a)
	$(2.0\pm1.0)\times10^{-3}$	water-ice	228		
	$>(6.0\pm2.0)\times10^{-2}$	60% H_2SO_4	228		

Comments

(a) Flow tube study (1 Torr He) using moveable injector and quadrupole MS sampling (HOBr at m/e 96, 98). The HOBr was generated *in situ* inside a moveable injector tube by reaction of Br_2 with OH that was produced from NO_2 + H from a microwave discharge of H_2 in He. The ice film was prepared by wetting the flow tube wall and rapidly cooling to 228 K. The uptake coefficient was measured by observation of the HOBr disappearance with injector position. The characteristic HOBr concentration for the uptake study on pure ice was $<5\times10^{11}$ molecule cm^{-3}. For concentrations exceeding 10^{12} molecule cm^{-3} a bimolecular rate law for HOBr disappearance was observed with no gas-phase products observed. There was no evidence for reversible adsorption of HOBr on ice. For the uptake on 60% H_2SO_4 the HOBr concentration was $<5\times10^{12}$ molecule cm^{-3}.

References

[1] J. P. D. Abbatt, Geophys. Res. Lett. **21**, 665 (1994).

HNO_3 + Substrate (water ice, water droplets, H_2SO_4/H_2O, salt surfaces)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
	Sulfate/H_2SO_4 (liquid) Substrates				
γ_{ss}	2.0×10^{-3}	75% H_2SO_4	230	Tolbert, Rossi, and Golden, 1988[1]	(a)
	4×10^{-3}	96.5% H_2SO_4	295		
γ_0	$(2.5\pm0.5)\times10^{-1}$	15–87% H_2SO_4	188	Reihs, Golden, and Tolbert, 1990[2]	(b)
	$(7.0\pm1.0)\times10^{-2}$	15–87% H_2SO_4	223		
γ	$(1.1\pm0.1)\times10^{-1}$	73% H_2SO_4 droplets	283	Van Doren *et al.*, 1991[3]	(c)
	Sulfate/H_2SO_4 (solid) Substrates				
γ_{ss}	$\geqslant3.0\times10^{-1}$	57.7% H_2SO_4	191.5	Hanson, 1992[4]	(d)
	$\geqslant2.0\times10^{-1}$	57.7% H_2SO_4	200		
	HNO_3-H_2O Substrates				
γ_{ss}	$\geqslant3.0\times10^{-1}$	ice film, HNO_3 coverage $\leqslant0.3$	191.5	Hanson, 1992[4]	(e)
	$\geqslant2.0\times10^{-1}$	ice film, HNO_3 coverage $\leqslant0.2$	200		
γ_{ss}	$4.0\times10^{-1}\leqslant\gamma\leqslant1.0$	NAT	197	Middlebrook *et al.*, 1992[5]	(f)
	H_2O (solid) Substrates				
γ_{ss}	$0.3^{+0.7}_{-0.1}$	ice film	197	Leu, 1988[6]	(g)
	H_2O (liquid) Substrates				
γ	$(7.1^{+2.0}_{-1.7})\times10^{-2}$	H_2O droplets	293	Van Doren *et al.*, 1990[7]	(h)
γ	$(1.93^{+0.21}_{0.15})\times10^{-1}$	H_2O droplets	268		
γ	$\leqslant1.0\times10^{-2}$	liquid jet	298	Kirchner *et al.*, 1990[8]	(i)
γ	$(1.1\pm0.1)\times10^{-1}$	H_2O droplets	298	Ponche, George, and Mirabel, 1993[9]	(j)
	Other Substrates				
γ_0	$(2.8\pm0.3)\times10^{-2}$	dry NaCl, KCl, NaBr, KBr, $NaNO_3$	300	Fenter, Caloz, and Rossi, 1994[10]	(k)
γ_0	$(1.0\pm0.2)\times10^{-2}$	dry $CaCO_3$, Na_2CO_3, rh$\leqslant$1%	300	Fenter, Caloz, and Rossi, 1995[11]	(l)
γ_0	$(4.0\pm2.0)\times10^{-4}$	single crystal NaCl, dry	300	Laux, Hemminger, and Finlayson-Pitts, 1994[12]	(m)

Comments

(a) Uptake experiment in a Knudsen cell flow reactor coupled to a modulated molecular beam sampled electron-impact MS. The bulk substrate (1–5 mL) was cooled slowly to temperatures of 210–230 K. The H_2SO_4 concentration in the bulk was obtained by dilution from 96.5% H_2SO_4 and was chosen to reflect the sulfuric acid aerosol concentration under stratospheric conditions, that is in the temperature range 210–230 K. The measured steady-state vapor pressure in the Knudsen cell was 4×10^{-4} Torr ($\pm30\%$). The listed γ values in the Table were measured under steady-state conditions. The apparent desorption temperature (probably an artifact) and yield of evaporated HNO_3 that was condensed on 75% H_2SO_4 at 230 K were measured to be 251 K and approximately 20%, respectively, in contrast to pure ice (230 K, 100%).

(b) The uptake was measured using the Knudsen cell technique with modulated electron-impact MS detection of HNO_3 vapor effusing out of the Knudsen cell. The sulfuric acid substrate was prepared from bulk solutions and cooled down to the temperature range 188–240 K. The values in the Table refer to γ measured at time zero (γ_0) before the uptake kinetics reaches steady state at the interfacial layer and thus become time independent. The time dependence of γ could be described by $1/\gamma(t)=\{1/\gamma_0+c(t)^{0.5}/4RTH^*(D)^{0.5}\}$ where D was the diffusion coefficient of HNO_3 in H_2SO_4 at temperature T. It results essentially from two competing factors: the solubility (Henry's law coefficient) of HNO_3 in sulfuric acid solution increases with decreasing temperature and H_2SO_4 concentration, and liquid diffusion of HNO_3 decreases with decreasing temperature. Accordingly, γ becomes time dependent for a H_2SO_4 concentration $\geqslant58\%$ at $T=223$ K and $\geqslant74\%$ at 188 K due to the fact that H^*D becomes sufficiently small. Effective Henry's law solubilities H^* were calculated whose temperature dependence resulted in heats of solvation and standard entropies of *solvation*. For H_2SO_4 concentrations $>58\%$ HNO_3 was dissolved in molecular form, thus $H=H^*$. For 58% H_2SO_4 the solubility data show a possible influence of ionic dissociation of HNO_3.

(c) Uptake experiment on fast droplet train (200 μm diameter 73% H_2SO_4 H_2O droplets) traversing a flow tube coupled to a multiple pass IR diode laser absorption cell of 728 cm optical path at pressures of 10 Torr and droplet-gas interaction times of 1–2 ms. HNO_3 is a confirmed reaction product of the heterogeneous N_2O_5-H_2O interaction and the product branching ratio defined as the ratio of observable HNO_3(g) and twice the depletion of N_2O_5(g) $[(HNO_3(g))/2\Delta(N_2O_5(g))]$ varies between 0.25 and 0.37 for interaction times of 1.1 to 1.6 ms, respectively. The value for γ listed in the Table has been corrected for gas phase diffusion and distortion of the Maxwellian velocity distribution and an adsorbing surface. Both the reduction in the HNO_3 uptake coefficient relative to that on water and the HNO_3 gaseous evolution from N_2O_5 uptake can be explained by the limited HNO_3 solubility in aqueous sulfuric acid.

(d) Uptake experiment in a frozen liquid-coated flow tube (~0.45 Torr He) coupled to a chemical ionization MS. Both the H_2O and HNO_3 signals were calibrated, and the volumetrically prepared 57.7% H_2SO_4 solution was applied on the inside of the flow tube wall at 205 K as a liquid. The $p(H_2O)$ corresponded to the ice point, and the pressure of HNO_3 was 8×10^{-8} Torr at 191.5 K and 3×10^{-7} Torr at 200 K. A correction was applied to the signal taking into account the steady state vapor pressure of p_{HNO_3} of $\sim10^{-8}$ Torr at 191.5 K and 200 K for HNO_3 coverages of 0.06 and 0.03, respectively. In the former case p_{HNO_3} was higher by a factor of three relative to the vapor pressure of NAT, in the latter case it was a factor of three lower than the NAT vapor pressure. With increasing coverage up to several monolayers the uptake coefficient stayed unchanged whereas the steady-state p_{HNO_3} increased by a factor of 10–20 relative to what is expected for NAT. With the HNO_3 and H_2O sources turned off, p_{HNO_3} slowly decreased from 5×10^{-8} Torr to 1.5×10^{-8} Torr over 40 minutes.

(e) Uptake experiment in an ice-coated flow tube (~0.45 Torr He) coupled to a chemical ionization MS. Both the H_2O and HNO_3 signals were calibrated with the $p(H_2O)$ at the ice point, and the pressure of HNO_3 set to 8×10^{-8} Torr at 191.5 K and 3×10^{-7} Torr at 200 K. A correction was applied to the signal taking into account the steady-state vapor pressure of p_{HNO_3} of $\sim10^{-9}$ Torr at 191.5 K and of $\sim10^{-8}$ Torr at 200 K for HNO_3 coverages of <0.3 and <0.2, respectively. In both cases p_{HNO_3} was lower by a factor of three relative to the vapor pressure of NAT. With increasing surface coverage of HNO_3 the HNO_3 uptake decreased and the steady-state p_{HNO_3} increased significantly as the ice surface became coated with HNO_3. The steady-state p_{HNO_3} over an ice surface with a coverage of approximately 1 monolayer of HNO_3 was about a factor of five higher than the vapor pressure over NAT. With the sources of HNO_3 and H_2O turned off, p_{HNO_3} at steady state decreased steadily with time to a value close to the vapor pressure of NAT at 191.5 K and to approximately a factor of two below p_{NAT} at 200 K.

(f) Isothermal film growth experiment in a static chamber with time-dependent FTIR monitoring of optical density of depositing NAT film at 3371 cm^{-1}. Absolute calibration of the thickness of the NAT deposited film was performed by observing the optical interference (fringes) in the range 4000 to 7000 cm^{-1} assuming a refractive index of 1.45 for NAT. The pressures were chosen so as to simulate stratospheric conditions with $p(H_2O)=1.5\times10^{-4}$ Torr and $p_{HNO_3}=(4-10)\times10^{-7}$ Torr. The spread of the γ values given in the Table corresponds to the range in the HNO_3 pressure. A doubling of the H_2O and the upper limit of the HNO_3 pressure left the uptake coefficient unchanged.

(g) Uptake experiment performed in a fast flow tube reactor with electron-impact MS sampling. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total). Owing to the large value of γ a diffusion correction had to be applied to the uptake rate coefficient using estimated diffusion coefficients of HNO_3 in He scaled to 197 K.

(h) Uptake experiment on a fast droplet train (200 μm diameter) crossing a flow tube in transverse geometry. Trace gas analysis is by IR diode laser absorption in a multiple pass cell of 728 cm optical path at total pressures of 5–20 Torr. Values listed are corrected for gas phase diffusion and distortion of velocity vector owing to rapid uptake.

(i) Uptake experiment involving the interaction of HNO_3 in an atmospheric pressure of synthetic air with a liquid jet of pure water. The uptake kinetics were studied by analyzing the liquid water content for NO_3^- or Cl^- using ion chromatography. The jet diameter was 90 μm, the jet length between 0.2 and 6 mm leading to contact times of 0.03 to 1.0 ms. The uptake coefficient was interpreted as a mass accommodation coefficient after fitting of the concentration of anions in the collected sample with the jet length taking into account the diffusion coefficients for the gas and liquid phase as well as the Henry's law constants. The results are regarded as lower limits owing to uncertainties in the velocity distribution of the liquid jet. The HNO_3 concentration was about 60 ppm and a measurement of γ relative to the one for HCl ($\gamma=1.0\times10^{-2}$) agreed with the absolute measurement of γ.

(j) Uptake experiment on a monodisperse (70–110 μm diameter droplets) and fast moving (480–2000 cm s^{-1}) droplet train propagating axially in a low-pressure flow tube in the pressure range 35–70 Torr. The contact time of the flowing gas interacting with the droplet train over a length of 7.5 to 21.5 cm varied between 3.7 and 45 ms. The extent of the uptake is determined by chemical analysis (ion chromatography) of collected aqueous phase. The uptake coefficient has been found to be independent of pH in the basic range, of the contact time and of the HNO_3 concentration in the range 10–100 ppm. The value listed in the Table has been corrected for gas phase diffusion as the experimentally determined uptake coefficient has been found to depend on pressure. The measured average uptake coefficient γ_{obs} is $(5.0\pm0.9)\times10^{-2}$ at 50 Torr N_2 and 298 K.

(k) Uptake experiment of HNO_3 on dry alkali salt powders (NaCl, NaBr, KCl, KBr) and $NaNO_3$ in a two-chamber low- pressure reactor (Knudsen cell) with modulated molecular beam sampling and phase sensitive detection using an electron-impact quadrupole MS. Both steady-state experiments with HNO_3 flows ranging from 10^{13} to 2×10^{15} molecule s^{-1} as well as transient dosing experiments ($\sim10^{14}$ molecules per pulse representing a few percent of a monolayer on the geometric surface of the sample) using a pulsed valve were performed. Both types of experiments were interpreted using a simple chemical kinetic model. The initial uptake coefficient γ_0 was measured in the low dose limit and was found to be dependent only on the external (geometric) surface, but independent of the nature of the salt, whereas the rate of HCl and HBr generation as well as the yield were found to be sensitive to several experimental parameters such as the nature, mass and grain size of the salt. The yields of HCl were in general higher than the yields of HBr. No synergistic effect in the HNO_3 uptake was observed in the presence of water vapor in the mTorr range. The adsorbed product hydrohalogenic acids are efficiently displaced from their sites of generation by HNO_3.

(l) Uptake experiment of HNO_3 on dry carbonate powders including a ''natural'' limestone in a two-chamber low pressure reactor (Knudsen cell) with modulated molecular beam sampling and phase sensitive detection using an electron-impact quadrupole MS. Both the uptake of HNO_3 as well as the generation of CO_2 and H_2O were measured for the heterogeneous chemical reaction $CaCO_3+2HNO_3\rightarrow Ca(NO_3)_2 + CO_2 + H_2O$ at flow rates of HNO_3 in the range 5×10^{14} to 6×10^{15} molecule s^{-1}. The uptake of HNO_3 shows an onset of saturation on the time scale of several minutes. The time evolution for all of the observed species points to a complex mechanism on the surface of or within the powder sample. The interaction of H_2O vapor on dry calcite powder is surprisingly strong and corresponds to an uptake coefficient γ_0 of 0.05 ± 0.02 for a flow rate of 1.7×10^{15} molecule s^{-1} with some signs of saturation on the time scale of a few minutes. The adsorption of HNO_3 on calcite seems to be independent of the H_2O partial pressure whereas the formation of H_2O and CO_2 seem to be enhanced by a factor of two in the presence of a flow of H_2O comparable to HNO_3.

(m) The reaction was followed by using x-ray photoelectron spectroscopic signals (XPS) quantifying the surface Cl^- and NO_3^- concentration as a function of exposure of a single crystal NaCl sample (100 face) to dry HNO_3 dispensed from a capillary mounted 1 mm in front of the dry salt sample under UHV conditions. The average sticking coefficient was obtained by dividing the number of nitrate species on the surface at saturation by the number of HNO_3 molecules incident on the sample. The assumption was made that at saturation, that is when the XPS signal due to N and O stopped changing with exposure time, the sample had acquired one monolayer of nitrate at the expense of the chloride. At saturation the Cl signal also reached a constant value having decreased by 50% compared to the original clean NaCl sample. The XPS signals (peak areas) were corrected for charging effects, properly background subtracted and scaled using standard XPS sensitivity factors.

Preferred Values

The uptake coefficient γ interpreted as mass accommodation coefficient α on *liquid* sulfuric acid at 200 K is found to be large, of the order of 0.2. It is weakly dependent on temperature over the range 188–223 K but independent of the sulfuric acid concentration in the range 15–87%. On sulfuric acid *droplets* γ (or α) attains similar values (0.1) at 283 K on 73% sulfuric acid. This confirms a trend where the accommodation coefficient on droplets seems to be larger than the limiting uptake coefficient for the corresponding bulk phase after suitable correction for saturation and temperature, where applicable. An equally large γ of 0.2 has been observed for *frozen* substrates of H_2SO_4.

On water ice γ is $\geqslant0.3$ at 200 K. This also seems to hold for NAT-like surfaces. On liquid water γ is interpreted as a mass accommodation coefficient and seems to be 0.1 at ambient temperature.

References

[1] M. A. Tolbert, M. J. Rossi, and D. M. Golden, Geophys. Res. Lett. **15**, 847 (1988).

[2] C. M. Reihs, D. M. Golden, and M. A. Tolbert, J. Geophys. Res. **95**, 16545 (1990).

[3] J. M. Van Doren, L. R. Watson, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. **95**, 1684 (1991).

[4] D. R. Hanson, Geophys. Res. Lett. **19**, 2063 (1992).

[5] A. M. Middlebrook, B. G. Koehler, L. S. McNeill, and M. A. Tolbert, Geophys. Res. Lett. **19**, 2417 (1992).

[6] M.-T. Leu, Geophys. Res. Lett. **15**, 17 (1988).

[7] J. M. Van Doren, L. R. Watson, P. Davidovits, D. R. Worsnop, M. Zahniser, and C. E. Kolb, J. Phys. Chem. **94**, 3265 (1990).

[8] W. Kirchner, F. Welter, A. Bongartz, J. Kames, S. Schweighoefer, and U. Schurath, J. Atmos. Chem. **10**, 427 (1990).

[9] J. L. Ponche, C. George, and P. Mirabel, J. Atmos. Chem. **16**, 1 (1993).

[10] F. F. Fenter, F. Caloz, and M. J. Rossi, J. Phys. Chem. **98**, 9801 (1994).

[11] F. F. Fenter, F. Caloz, and M. J. Rossi, Atmos. Environ. in press (1995).

[12] J. M. Laux, J. C. Hemminger, and B. J. Finlayson-Pitts, Geophys. Res. Lett. **21**, 1623 (1994).

HONO + Substrate (water droplets and liquid jet)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	5.0×10^{-3}	liquid jet	299	Kirchner *et al.*, 1994[1]	(a)
γ	$0.05^{+0.02}_{-0.01}$	liquid jet	297	Bongartz *et al.*, 1994[2]	(b)
	$0.05^{+0.04}_{-0.01}$	droplets	245		

Comments

(a) Uptake experiment involving the interaction of HONO in an atmospheric pressure of synthetic air with a liquid jet of pure water. The uptake kinetics were studied by analyzing the liquid water content for NO_2^- using ion chromatography. The jet diameter was 90 μm, the jet length between 0.2 and 6 mm leading to contact times of 0.03 to 1.0 ms. The uptake coefficient was interpreted as a mass accommodation coefficient after fitting of the concentration of anions in the collected sample with the jet length taking into account the diffusion coefficients for the gas and liquid phase as well as the Henry's law constants. The results are regarded as lower limits owing to uncertainties in the velocity distribution of the liquid jet. The gas phase interacting with the liquid jet consisted of approximately 130 ppm of HONO detected using UV absorption, 170 ppm of NO_2 detected using LIF excited at 442 nm and an unknown amount of NO. Similar amounts of pure NO_2 in air do not lead to detectable amounts of NO_2^- after liquid jet interaction. Using an effective Henry's law constant that takes into account the pK_a of HONO and an acid dissociation constant of $k_a = 5.0 \times 10^6$ s^{-1} results in satisfactory fits to the NO_2^- concentration vs. time curves if the UV absorption cross section of HONO is reduced by 30%.

(b) This work on HONO uptake on liquid condensed surfaces comprised two experimental techniques related to flowing gas experiments: an improved version of the liquid jet and the droplet train technique. The liquid jet technique involved the measurement of the concentration of NO_2^- in the collected jet. The jet diameter was 110 μm at the orifice leading to contact times between 0.1 to 0.8 ms at one atmosphere of N_2. The droplet train technique involved exposing gasphase HONO at pressures of 30–60 Torr to a fast moving train of droplets of 100–110 μm diameter at residence times of 3.7–16 ms. The small partial pressure of H_2O of 0.25 Torr corresponded to a droplet surface temperature of 245±5 K. The first value of the uptake coefficient in the Table corresponds to the measurement using the liquid jet technique where the error limits have been estimated from a sensitivity analysis of the input parameters used to fit the concentration in the collected liquid vs. contact time data. The principal source of uncertainty is the evaluation of the binary gas-phase diffusion coefficient of HONO (D_p). The second value of the uptake coefficient in the Table pertains to the application of the fast droplet train method. The observed uptake coefficient was independent of reaction time but dependent on total pressure. Again, a 20% uncertainty in D_p leads to the stated error intervals.

References

[1] W. Kirchner, F. Welter, A. Bongartz, J. Kames, S. Schweighoefer, and U. Schurath, J. Atmos. Chem. **10**, 427 (1990).
[2] A. Bongartz, J. Kames, U. Schurath, C. George, P. Mirabel, and J. L. Ponche, J. Atmos. Chem. **18**, 149 (1994).

NO + Substrate (water ice, 70% H_2SO_4-H_2O-ice)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$<1.0\times10^{-4}$	H_2O-ice	195	Leu, 1988[1]	(a)
γ_0	$\leq5.0\times10^{-6}$	70% H_2SO_4	193–243	Saastad, Ellermann, and Nielsen, 1993[2]	(b)

Comments

(a) Uptake experiment in an ice-coated flow tube coupled to electron-impact MS. The ice film was deposited from water vapor.

(b) Measurement of the total pressure drop in a static system over bulk frozen 70% H_2SO_4/H_2O monitored by MS. Visual inspection of the substrate indicated a supercooled glass even at the lowest temperatures. The values given represent conservative upper limits derived in comparison with calculated signals. Three kinds of experiments were performed: uptake of NO, NO_2, and a mixture of NO-NO_2, all giving the same result.

References

[1] M.-T. Leu, Geophys. Res. Lett. **15**, 851 (1988).
[2] O. W. Saastad, T. Ellermann, and C. J. Nielsen, Geophys. Res. Lett. **20**, 1191 (1993).

NO_2 + Substrate (water ice and droplets, 70% H_2SO_4-H_2O-ice)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$<1.0\times10^{-4}$	H_2O-ice	195	Leu, 1988[1]	(a)
γ_0	$(6.3\pm0.7)\times10^{-4}$	H_2O droplets	273	Lee and Tang, 1988[2]	(b)
γ_0	$\leq5.0\times10^{-6}$	70% H_2SO_4	193–243	Saastad, Ellermann, and Nielsen, 1993[3]	(c)
γ_{obs}	$(1.5\pm0.8)\times10^{-3}$	H_2O droplets	298	Ponche, George, and Mirabel, 1993[4]	(d)

Comments

(a) Uptake experiment in an ice-coated flow tube coupled to electron-impact MS. The ice film was deposited from water vapor.

(b) Uptake experiment involving a stopped flow of NO_2 in humidified He carrier gas exposed to a circulating fluid sample of water containing between 1×10^{-2} and 7×10^{-2} M of hydroquinone as a scavenger in basic solution. Total pressures of 25–50 Torr were used and the uptake coefficients were corrected for gas phase diffusion resulting in mass accommodation coefficients. A 10% change in the diffusion coefficient for NO_2 in He resulted in a variation between 2% and 20% of the accommodation coefficient.

(c) Measurement of the total pressure drop in a static system over bulk frozen 70% H_2SO_4-H_2O monitored by MS. Visual inspection of the substrate indicated a supercooled glass even at the lowest temperatures. The values given represent conservative upper limits derived in comparison with calculated signals. Three kinds of experiments were performed: uptake of NO, NO_2, and a mixture of NO-NO_2, all giving the same result.

(d) Uptake experiment on a monodisperse (70–110 μm diameter droplets) and fast moving (480–2000 cm s^{-1}) droplet train propagating axially in a low-pressure flow tube in the pressure range 35–70 Torr. The contact time of the flowing gas interacting with the droplet train over a length of 7.5 to 21.5 cm varied between 3.7 and 45 ms. The extent of the uptake is determined by chemical analysis (ion chromatography) of collected aqueous phase. A chemical scavenger H_2O_2 was added to the condensed phase in order to scavenge NO_2^- to nitrate. The uptake coefficient has been found to be independent of pH in the range 4–11 and of the contact time. The observed value of the uptake coefficient seems to exceed the value expected on the basis of published Henry's law coefficients by at least a factor of ten and is attributed to unknown chemical reactions.

References

[1] M.-T. Leu, Geophys. Res. Lett. **15**, 851 (1988).
[2] J. H. Lee and I. N. Tang, Atmos. Environ. **22**, 1147 (1988).
[3] O. W. Saastad, T. Ellermann, and C. J. Nielsen, Geophys. Res. Lett. **20**, 1191 (1993).
[4] J. L. Ponche, C. George, and P. Mirabel, J. Atmos. Chem. **16**, 1 (1993).

$CH_3CO(O)_2NO_2$ (PAN) + Substrate (water jet)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$1.0\times10^{-3}<\gamma$ $<5\times10^{-3}$	liquid jet	281.8	Kirchner *et al.*, 1990[1]	(a)

Comments

(a) Uptake experiment involving the interaction of PAN in an atmospheric pressure of synthetic air with a liquid jet of pure water. The uptake kinetics were studied by analyzing the liquid water content for the sum of NO_2^- + NO_3^- using ion chromatography. The jet diameter was 90 μm, the jet length between 0.2 and 6 mm leading to contact times of 0.03–1.0 ms. The uptake coefficient was interpreted as a mass accommodation coefficient after fitting of the concentration of anions in the collected sample with the jet length taking into account the diffusion coefficients for the gas and liquid phase as well as the Henry's law constants. The results are regarded as lower limits owing to uncertainties in the velocity distribution of the liquid jet. The PAN concentration was about 290 ppm detected by UV absorption in the range 200–250 nm with small impurities of NO_2 (250 ppb) detected using LIF excited at 442 nm and CH_3ONO_2 (>3 ppm) detected by GC. The poor agreement between the absolute measurement and the determination of γ relative to the one for HCl ($\gamma=10^{-2}$) indicates a problem with the data reduction for low solubility gases.

References

[1] W. Kirchner, F. Welter, A. Bongartz, J. Kames, S. Schweighoefer, and U. Schurath, J. Atmos. Chem. **10**, 427 (1990).

NH_3 + Substrate (liquid water jet, water droplets)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$(4.0^{+3}_{-0.5})\times10^{-2}$	liquid jet	299±1	Bongartz *et al.*, 1995[1]	(a)
γ	$(9.7\pm0.9)\times10^{-2}$	H_2O droplets	290	Ponche, George, and Mirabel, 1993[2]	(b)

Comments

(a) Uptake experiment of NH_3 by a liquid jet of dilute HCl solution using a combination of a peristaltic pump/conductivity detector for the continuous on-line measurement of NH_4^+ in the collected jet waters. The liquid jet diameter was 97±2 μm, the jet length could be varied from 0.2 to 4 mm corresponding to a contact time of 0.1–0.8 ms. Both synthetic air and He were used as a carrier gas at a total pressure of 1 atm. The NH_3 concentration was in the range 100–200 ppm for air and 50–100 ppm for He as a carrier gas. Despite a factor of three difference in the diffusion coefficient for NH_3 gas the γ values for air as a carrier gas were agreeing very well with the ones measured in He ($\gamma = 3.5\times10^{-2}$ in air vs. 4.0×10^{-2} in He). The results are extremely sensitive to the value of the diffusion coefficient for NH_3 gas and sensitive to Henry's constant for NH_3. Owing to the short contact times the method is virtually free of saturation effects in the liquid phase.

(b) Uptake experiment on a monodisperse (70–110 μm diameter droplets) and fast moving (480–2000 cm s^{-1}) droplet train propagating axially in a low pressure flow tube in the pressure range 35–70 Torr. The contact time of the flowing gas interacting with the droplet train over a length of 7.5 to 21.5 cm varied between 3.7 and 45 ms. The extent of the uptake is determined by chemical analysis (ion chromatography) of collected aqueous phase. The uptake coefficient has been found to be independent of pH in the range 4.2– 11.5 but dependent on the contact time. The value listed in the Table has been corrected for gas phase diffusion as the experimentally determined uptake coefficient has been found to depend on pressure. The measured average uptake coefficient γ_{obs} is $(2.4\pm1.0)\times10^{-2}$ at 70 Torr N_2 and 290 K.

References

[1] A. Bongartz, S. Schweighoefer, C. Roose, and U. Schurath, J. Atmos. Chem. **20**, 35 (1995).

[2] J. L. Ponche, C. George, and P. Mirabel, J. Atmos. Chem. **16**, 1 (1993).

O_3 + Substrate (water ice, liquid, NAT, Pyrex)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$<1.0\times10^{-4}$	ice film	195	Leu, 1988[1]	(a)
γ_{ss}	$<1.0\times10^{-6}$	ice film	195	Dlugokencky and Ravishankara, 1992[2]	(b)
	$<1.0\times10^{-6}$	97% H_2SO_4	196		
	$(1-5)\times10^{-4}$	NAT	195		
γ_{ss}	$\geqslant2\times10^{-3}$	liquid water	276	Utter *et al.*, 1992[4]	(c)
γ_{ss}	$<6.0\times10^{-5}$	ice film, Pyrex	183	Kenner, Plumb, and Ryan, 1993[4]	(d)
	$<8.0\times10^{-5}$	NAT	183		

Comments

(a) Uptake experiment performed on an ice-coated flow tube coupled to electron impact MS. The ice film was deposited from water vapor.

(b) Uptake experiment in a coated flow tube reactor using chemiluminescent ozone detection (via reaction of $O_3 + NO \rightarrow NO_2^* + O_2$). The O_3 detection limit was $\sim2\times10^7$ molecule cm^{-3} at S/N=1 and 1.5 min averaging time. Typical pressures were $p_{O_3}=10^8-10^{12}$ molecule cm^{-3} with 1 Torr of He carrier gas. The flow tube was coated with the appropriate solution at $T \sim230$ K to result in a coating of approx. 2 mm thickness. No diffusion corections were deemed necessary at the low vapor pressure of H_2O (0.65 mTorr). Saturation phenomena were apparent in that use of low ozone concentrations ($\leqslant2\times10^9$ molecule cm^{-3}) resulted in the largest values of γ ($\sim1.0\times10^{-2}$) and increasing sulfite concentrations obtained still larger values for reactive uptake (0.01 on 0.1 M Na_2SO_3 at 196 K).

(c) Uptake experiment on wetted-wall flow tube reactor in which a film of liquid water (0.2 mm thickness) flowed down a vertical flow tube at a liquid flow velocity of 4–16 cm s^{-1}. The initial ozone concentration was 10^{11} molecule cm^{-3} and was detected at the exit of the flow tube using chemiluminescence. The gas flow characteristics was between laminar and turbulent and corrections had to be applied for significant radial O_3 concentrations gradients. The total pressure was between

10.2–11 Torr with half of it being H_2O vapor. No uptake was observed when ozone interacted with pure deionized water presumably owing to saturation effects. Adding a trapping agent for ozone such as Na_2SO_3, $Na_2S_2O_3$, or $SnCl_2$ increased γ as a function of the concentration of the trapping agent to values in the 10^{-2} range. The uptake rate constant was independent of changes in the liquid flow velocity by a factor of four and of the gas flow velocity by a factor of three. A conservative lower limit for the accommodation coefficient of 2×10^{-2} is obtained.

(d) Uptake experiment in a fast flow tube reactor with electron-impact MS sampling and ion counting. The cryogenic phase was deposited from H_2O vapor and H_2O:HNO_3=3:1 vapor mixtures to obtain thicknesses of 4–7 μm for ice and additional 2–3 μm thick films on top of already deposited ice layers. This limitation in terms of deposited material could lead to an increase of γ by a factor of two at most. Taking into account the porosity of the deposited layer would lead to a lowering of γ.

References

[1] M.-T. Leu, Geophys. Res. Lett. **15**, 851 (1988).

[2] E. Dlugokencky and A. R. Ravishankara, Geophys. Res. Lett. **19**, 41 (1992).

[3] R. G. Utter, J. B. Burkholder, C. J. Howard, and A. R. Ravishankara, J. Phys. Chem. **96**, 4973 (1992).

[4] R. D. Kenner, I. C. Plumb, and K. R. Ryan, Geophys. Res. Lett. **20**, 193 (1993).

Cl_2 + Substrate (water ice)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$<10^{-4}$	ice film	200	Leu, 1988[1]	(a)
γ_{ss}	$<5.0\times10^{-5}$	ice film	183	Kenner, Plumb, and Ryan, 1993[2]	(b)

Comments

(a) Uptake experiment performed in a fast flow tube reactor using electron-impact MS sampling. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total). The value given in the Table is an upper limit.

(b) Fast flow tube reactor study using electron-impact MS sampling and ion counting. The cryogenic phase was deposited from H_2O vapor to obtain thicknesses of 4–7 μm. This limitation in terms of deposited material could lead to an increase of γ by a factor of two at most. Taking into account the porosity of the deposited layer would lead to a lowering of γ.

References

[1] M.-T. Leu, Geophys. Res. Lett. **15**, 17 (1988).

[2] R. D. Kenner, I. C. Plumb, and K. R. Ryan, Geophys. Res. Lett. **20**, 193 (1993).

ClO + Substrate (water ice, H_2SO_4-H_2O, NAT, Pyrex)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$(8.0^{+14}_{-5})\times10^{-4}$	70% H_2SO_4	220	Martin, Judeikis, and Wun, 1980[1]	(a)
γ_{ss}	$>1.0\times10^{-2}$	ice film	190	Leu, 1988[2]	(b)
γ_{sss}	$<1.8\times10^{-5}$	Pyrex	295	Kenner, Plumb, and Ryan, 1993[3]	(c)
	$(8\pm2)\times10^{-5}$	Pyrex, ice film, and NAT	183		

Comments

(a) Measurement of the uptake kinetics in a fast flow tube with EPR detection of ClO. Pure Cl_2 at 0.5 Torr was discharged in a microwave cavity and combined downstream with an excess of O_3 in order to generate ClO. The quartz flow tube was coated with halocarbon wax and the discharge tube with solid B_2O_3 in order to minimize wall losses of ClO. The inside of the flow tube was coated with H_2SO_4 and the H_2O vapor pressure was held constant throughout the temperature range at 5×10^{-4} Torr leading to a changing composition of the H_2SO_4-H_2O mixture as the temperature was changed (96% at 300 K, 80% at 240 K). Therefore no separation between the effects of changing composition of the cryogenic phase (considered to be negligible) and the temperature dependence of γ could be achieved. All kinetic results were obtained from the full numerical integration of the parabolic flow system including axial diffusion and resulted in a pronounced negative temperature dependence of the uptake coefficient γ_{ss} represented by $\ln\gamma_{ss}=\{-9.361+(3.22\pm1.34)\times(1000/T-3.840)\}$ on H_2SO_4 at T=240–295 K. The product of the heterogeneous reaction was HCl and no effect on γ upon irradiation by simulated sunlight was found within a $\pm 20\%$ variation of γ.

(b) Uptake experiment performed in a fast flow tube reactor using electron-impact MS sampling. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total). The value given in the Table is a lower limit.

(c) Uptake experiment performed in a fast flow tube reactor using electron-impact MS sampling and ion counting at m/e 51. The cryogenic phase was deposited from H_2O vapor and $H_2O:HNO_3=3:1$ vapor mixtures to obtain thicknesses of 4–7 μm for ice and additional 2–3 μm thick films on top of already deposited ice layers. This limitation in terms of deposited material could lead to an increase of γ by a factor of two at most. The ClO free radical was generated either from a microwave discharged mixture of $Cl_2 + O_2$ in He or from a discharged Cl_2-He mixture in an excess of O_3 resulting in typical densities of $(2-3)\times 10^{11}$ molecule cm^{-3}. The kinetic results were independent of the ClO densities varied by a factor of ten. The error limit for γ on NAT is twice that for water-ice.

References

[1] L. R. Martin, H. S. Judeikis, and M. Wun, J. Geophys. Res. **85**, 5511 (1980).

[2] M.-T. Leu, Geophys. Res. Lett. **15**, 851 (1988).

[3] R. D. Kenner, I. C. Plumb, and K. R. Ryan, Geophys. Res. Lett. **20**, 193 (1993).

Cl + Substrate (SiO_2, H_2SO_4-H_2O, Teflon)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	1.0×10^{-3}	acid-treated SiO_2	300	Martin, Judeikis, and Wun, 1980[1]	(a)
	2.0×10^{-3}	base-treated SiO_2	300		
	1.0×10^{-4}	H_2SO_4 conc, 5.0×10^{-4} NH_4SO_4	300		
γ_{ss}	$(5.9^{+3.1}_{-2.4})\times 10^{-4}$	70% H_2SO_4	220	Martin, Judeikis, and Wun, 1980[1]	
γ_{ss}	$\leq 6.0\times 10^{-6}$	PTFE-Teflon, for Cl,Cl*	300	Müller-Markgraf and Rossi, 1990[2]	(b)

Comments

(a) Measurement of the uptake kinetics in a fast flow tube with EPR detection of Cl. A 1% Cl_2 in He mixture at 1.5–2.0 Torr or pure Cl_2 at 0.25 Torr was discharged in a microwave cavity at 20 W in order to generate Cl. The quartz flow tube was coated with halocarbon wax and the discharge tube with solid B_2O_3 in order to minimize wall losses of Cl. The inside of the flow tube was coated with H_2SO_4 and the H_2O vapor pressure was held constant throughout the temperature range at 5×10^{-4} Torr leading to a changing composition of the H_2SO_4-H_2O mixture as the temperature was changed (96% at 300 K, 71% at 221 K). Therefore no separation between the effects of changing composition of the cryogenic phase (considered negligible) and the temperature dependence of γ could be achieved. All kinetic results were obtained from the full numerical integration of the parabolic flow and the chemical mechanism including axial diffusion. It resulted in a slight negative temperature dependence of the uptake coefficient γ represented by $\ln\gamma_{ss}=\{-8.874+(2.122 \pm 0.78)\times(1000/T-3.867)\}$ on H_2SO_4 at $T=221-296$ K. The product of the heterogeneous reaction was HCl and no effect on γ upon irradiation by simulated sunlight was found within a $\pm 20\%$ variation of γ.

(b) The uptake kinetics of both ground state $Cl(^2P_{3/2})$ and upper spin-state $Cl^*(^2P_{1/2})$ were studied in a low-pressure flow reactor (Knudsen cell) using Resonance-Enhanced Multiphoton Ionization ([3 + 2] REMPI) detection at 404.02 and 405.3 nm for Cl and Cl* detection, respectively. The Cl was added to the reactor through a pulsed valve-microwave discharge combination using Cl_2-He gas mixtures (1:2) undergoing from 25 to 40% decomposition at 70 W absorbed power. The decomposition of the parent Cl_2 was monitored by electron-impact MS thus affording a quantitative calibration of the REMPI signal. Typically, 10^{15} molecules per pulse were obtained leading to densities of 5×10^{12} molecule cm^{-3}. Depending on the discharge conditions, comparable densities of Cl* were generated showing identical (slow) uptake kinetics on laboratory Teflon surfaces. Thus the lifetime for both Cl and Cl* at densities of 10^{12} molecule cm^{-3} is of the order of several seconds.

References

[1] L. R. Martin, H. S. Judeikis, and M. Wun, J. Geophys. Res. **85**, 5511 (1980).

[2] W. Müller-Markgraf and M. J. Rossi, Rev. Sci. Instrum. **61**, 1217 (1990).

Br + Substrate (Teflon)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$(5.6\pm1.5)\times10^{-5}$	PTFE Teflon, for Br, Br*	300	Müller-Markgraf and Rossi, 1995[1]	(a)

Comments

(a) The uptake kinetics of both ground state Br ($^2P_{3/2}$) and upper spin-state Br*($^2P_{1/2}$) has been studied in a low-pressure Knudsen cell using Resonance-Enhanced Multiphoton Ionization ([3+2] REMPI) detection at 461.9 and 459.1 nm, respectively. The Br was added to the reactor through a pulsed valve-microwave discharge combination using pure Br_2 undergoing 8% decomposition at 30 W absorbed power. The decomposition of the parent Br_2 was monitored at m/e 160 using electron-impact MS thus affording a quantitative calibration of the REMPI signal. The detection limit for Br was estimated as 5×10^{10} cm^{-3} for a signal to noise ratio of 2:1. Depending on the discharge conditions, comparable densities of Br* were generated showing identical uptake kinetics on laboratory Teflon surfaces if a correction was made for the radiative lifetime of Br* (0.77 s).

References

[1] W. Müller-Markgraf and M. J. Rossi, Int. J. Chem. Kinet. **27**, 403 (1995).

SO_2 + Substrate (water droplets and jet)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$(5.4\pm0.5)\times10^{-2}$	water droplets, pH=11.5	295	Gardner *et al.*, 1987[1], 1989[2]	(a)
γ	$(1.1\pm0.2)\times10^{-1}$	water droplets	273	Worsnop *et al.*, 1989[3]	(b)
γ	8.0×10^{-3}	effective H_2O droplet, pH=1	283	Jayne *et al.*, 1990[4]	(c)
	1.1×10^{-1}	effective H_2O droplet, pH=6			
γ	$(6.0^{+1.4}_{-3})\times10^{-2}$	liquid jet	300	Welter, Schweighoefer, and Schurath, 1990[5]	(d)
γ	$(1.3\pm0.1)\times10^{-1}$	water droplets	298	Ponche, George, and Mirabel, 1993[6]	(e)

Comments

(a) Uptake experiment on a fast moving droplet train propagating in a flow tube coupled to tunable diode laser absorption of SO_2 in a multiple pass absorption cell (728 cm optical path). The measurement consisted of monitoring the gas density in the flow tube with the droplet train switched on and off. The droplet size varied from 80–180 μm and the residence time of the individual droplet ranged from 2.2 to 12.8 ms. The SO_2 density was $(1.5-15)\times10^{12}$ molecule cm^{-3} and the total pressure was 21 Torr (He + H_2O). A small admixture of CH_4 was used to control the degree of water saturation (100%) of the carrier gas in order to prevent evaporation/condensation of the water droplets. The listed value has been corrected for gas-phase diffusion of SO_2 towards the droplet surface. When mass transport limitations in the condensed phase due to liquid diffusion and boundary layer saturation (Henry's law) are taken into account, the observed value is consistent with a value of γ=0.12 for a 120 μm diameter droplet. This discrepancy is due to evaporation of initially adsorbed SO_2.

(b) Uptake experiment on a fast moving neutral water droplet train propagating in a flow tube either in axial or transverse direction. The interaction time ranged from 2 to 12 ms (axial) or from 0.5 to 2 ms (transverse), and the temperature was varied from 260 to 292 K at total pressures from 10 to 50 Torr (He + H_2O) for the axial configuration, and 2.3 to 10 Torr for the transverse geometry. A tunable diode laser was used to measure the absorption of SO_2 in a multiple pass absorption cell (728 cm optical path) which was appended to the droplet flow tube. Initial SO_2 densities were of the order of 10^{13} molecule cm^{-3}. The measurement consists of monitoring the gas density in the multiple path absorption cell with the droplet train switched on and off and calculating an observed value of γ. A slight negative temperature dependence for the SO_2 uptake was obtained with $E=(2\pm5)$ kJ mol^{-1}.

(c) Uptake experiment on a fast moving droplet train propagating in a flow tube either in axial or transverse direction. The interaction time ranged from 2 to 12 ms (axial) or from 0.5 to 2 ms (transverse), and the temperature was varied from 275 to 285 K at total pressures from 5 to 10 Torr (He + H_2O). A tunable diode laser was used to measure the absorption of SO_2 in a multiple pass absorption cell (728 cm optical path) which was appended to the droplet flow tube. Initial densities of SO_2 in the range $10^{13}-10^{15}$ molecule cm^{-3} were used. The measurement consists of monitoring the gas density in the multiple path absorption cell with the droplet train switched on and off. The pH in the bulk droplets ranged from 0 to 12 and corrections for gas phase diffusion and additional acidification of the droplet owing to SO_2 adsorption were applied to the uptake kinetics. The results displayed in the Table were obtained at a minimal droplet gas interaction time and a minimal SO_2 density of 10^{13} molecule cm^{-3}. Taking into account liquid diffusion of SO_2 and the kinetics of ionic dissociation of SO_2 in H_2O, a γ value of 0.11 is obtained at low (effective) pH. This value is observed at pH>5 (effective pH within the diffusion depth) and is significantly smaller than 1, the assumed mass accommodation coefficient. The discrepancy is attributed to evaporation of initially adsorbed SO_2. The measured uptake kinetics are consistent only with a larger value of the rate constant for ionic solvation which is attributed to the formation of an incipient complex H^+-HSO_3^- in the interface region.

(d) Uptake experiment of SO_2 in an atmosphere of synthetic air with a liquid jet of pure water to which small amounts of H_2O_2 were added in order to afford rapid oxidation of SO_2 to sulfate. The uptake kinetics of typically 100 ppm SO_2 in synthetic air were measured by analyzing the sulfate concentration in the collected jet waters using ion chromatography. The jet was emerging out of a capillary of 100 μm diameter and gas/jet contact times were between 0.03 to 1.0 ms. The uptake coefficient was interpreted as a mass accommodation coefficient after fitting of the concentration of sulfate in the collected sample with the jet length taking into account the diffusion coefficients for the gas and liquid phase as well as the Henry's law constants. The uptake was found to be dependent on SO_2 concentration owing to a change in surface pH. Addition of NH_3 to the SO_2-air mixture minimized the pH dependence. The true surface velocity of the liquid jet was taken from analogous jets described in the literature and an extreme sensitivity of γ on the gas diffusion coefficient for SO_2 was noted.

(e) Uptake experiment on a monodisperse (70–110 μm diameter droplets) and fast moving (480–2000 cm s^{-1}) droplet train propagating within a low-pressure flow tube in the pressure range 35–70 Torr. The contact time of the flowing gas interacting with the droplet train over a length of 7.5 to 21.5 cm varied between 3.7 and 45 ms. The extent of the uptake was determined by chemical analysis (ion chromatography) of collected aqueous phase. A chemical scavenger H_2O_2 was added to the condensed phase in order to trap dissolved SO_2 by rapid chemical reaction to H_2SO_4. The observed uptake coefficient was strongly dependent on the pH of the droplet in the range 4–11 and on the interaction time. The average value of the uptake coefficient γ_{obs} is $(6.0\pm0.8)\times10^{-2}$ at 38 Torr N_2, 298 K and pH 11, a value to which the others determined at lower pH converge. The value given in the Table has been corrected for gas-phase diffusion.

References

[1] J. A. Gardner, L. R. Watson, Y. G. Adewuyi, P. Davidovits, M. S. Zahniser, D. Worsonop, and C. E. Kolb, J. Geophys. Res. **92**, 10887 (1987).

[2] J. A. Gardner, L. R. Watson, Y. G. Adewuyi, J. M. Van Doren, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, *Bionic Sulfur in the Environment*, Am. Chem. Soc. Symp. Ser., Vol. 393, edited by E. S. Saltzman and W. J. Cooper (ACS, Washington, DC, 1989), pp. 504–517.

[3] D. R. Worsnop, M. S. Zahniser, C. E. Kolb, J. A. Gardner, L. R. Watson, J. M. Van Doren, J. T. Jayne, and P. Davidovits, J. Phys. Chem. **93**, 1159 (1989).

[4] J. T. Jayne, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. **94**, 6041 (1990).

[5] F. Welter, S. Schweighoefer, and U. Schurath, *The Proceedings of Eurotrac Symposium 90*, edited by P. Borrell *et al.* (SPB Academic Publishing, 1991), p. 335.

[6] J. L. Ponche, C. George, and P. Mirabel, J. Atmos. Chem. **16**, 1 (1993).

H_2O_2 + Substrate (water droplets)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$(3.2\pm0.2)\times10^{-1}$	droplets	260	Worsnop *et al.*, 1989[1]	(a)
	$(1.8\pm0.2)\times10^{-1}$	droplets	273		
	$(8.0\pm0.2)\times10^{-2}$	droplets	292		

Comments

(a) Uptake experiment on a fast moving water (pH=7) droplet train propagating in a flow tube either in axial or transverse direction. The interaction time ranged from 2 to 12 ms (axial) or from 0.5 to 2 ms (transverse), and the temperature was varied from 260 to 292 K at total pressures from 10 to 50 Torr (He + H_2O) for the axial configuration, and 2.3 to 10 Torr for the transverse geometry. A tunable diode laser was used to measure the absorption of H_2O_2 in a multiple pass absorption cell (728 cm optical path) which was appended to the droplet flow tube. Initial H_2O_2 densities were in the range $(1.5-15)\times10^{12}$ molecule cm^{-3}. The measurement consists of monitoring the gas density in the multiple path absorption cell with the droplet train switched on and off and calculating an observed value of γ. A negative temperature dependence for the H_2O_2 uptake was obtained with $E=-(26\pm7)$ kJ mol^{-1}.

References

[1] D. R. Worsnop, M. S. Zahniser, C. E. Kolb, J. A. Gardner, L. R. Watson, J. M. Van Doren, J. T. Jayne, and P. Davidovits, J. Phys. Chem. **93**, 1159 (1989).

CH_3COCH_3 + Substrate (water droplets)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$(6.6\pm1.2)\times10^{-1}$	droplets	263	Duan *et al.*, 1993[1]	(a)
	$(1.3\pm0.2)\times10^{-2}$	droplets	285		

Comments

(a) Uptake experiment on a fast monodisperse droplet train moving on axis in a flow tube and sampled by a quadrupole MS. The droplet diameter ranged between 50 to 200 μm and the total pressure in the flow tube was between 6 and 20 Torr. The droplet-acetone interaction time was between 1.8 and 21 ms and the partial pressure of water in the flow tube was adjusted to result in droplets ranging from the supercooled state to liquid. The values listed in the Table were corrected both for gas-phase diffusion which corresponded to a 20% correction of γ_{obs} at most, and solubility saturation (Henry's law). After correction of those two processes the experimental uptake coefficients were interpreted as mass accommodation coefficients α. The temperature dependence of α resulted in an enthalpy and entropy of solvation of 53.3 kJ mol^{-1} and -224.3 J mol^{-1} K^{-1}, respectively. A parametric representation of Henry's law constant for dissolution of acetone in pure water as a function of temperature was obtained ($H=30$ mol dm^{-3} atm^{-1} at 273 K).

References

[1] S. X. Duan, J. T. Jayne, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. **97**, 2284 (1993).

H_2CO + Substrate (water droplets, H_2SO_4/H_2O solution)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$(2.0\pm0.3)\times10^{-2}$	droplets	267	Jayne *et al.*, 1993[1]	(a)
γ_{ss}	1×10^{-2}	67% H_2SO_4 bulk	223	Tolbert *et al.*, 1993[2]	(b)
	8×10^{-2}	75% H_2SO_4bulk	223		

Comments

(a) Uptake experiment on a fast monodisperse droplet train moving axially in a flow tube and sampled by a differentially pumped quadrupole MS. The droplet diameter ranged between 80 to 240 μm and the total pressure in the flow tube was between 6 and 20 Torr N_2 with the formaldehyde density being in the range $10^{13}-10^{14}$ molecule cm^{-3}. The droplet-formaldehyde interaction time was between 1.8 and 21 ms. The partial pressure of water vapor in the flow tube was adjusted to result in droplets ranging from the supercooled state at 260 K to near ambient temperature at 290 K. The observed uptake coefficient was time independent but depended strongly on pH at the high end of the scale reflecting the pH dependence of the formation of the *gem*-diol in a base-catalyzed reaction. The dependence of γ_{obs} on OH^- activity resulted in a rate coefficient of $(4.0\pm0.2)\times10^7$ cm^3 mol^{-1} s^{-1} at 267 K for the reaction $H_2CO + H_2O \rightarrow H_2C(OH)_2$ and the dependence of γ_{obs} on sulfite activity at pH$-$10 obtained a rate coefficient of $(2.2 \pm 0.2)\times10^7$ cm^3 mol^{-1} s^{-1} at 267 K for the addition of SO_3^{2-} to H_2CO resulting in hydroxymethanesulfonate $[CH_2(O^-)SO_3^-]$.

(b) Uptake experiment of CH_2O on quiescent and stirred sulfuric acid solutions in a Knudsen cell flow reactor which is monitored by modulated molecular beam MS. The decrease of the CH_2O steady-state vapor pressure upon exposure to the low-temperature sulfuric acid solution whose concentration was determined by titration was monitored at m/e 29 as a function of exposure time. The concentration of CH_2O ranged from 2×10^{10} to 2×10^{11} molecule cm^{-3} and no new gas phase products were detected during the uptake. By analogy to known condensed phase kinetics CH_2O is both solvated to methyleneglycol as well as protonated. The uptake showed a negative temperature dependence over the range 205–234 K and a pronounced concentration dependence of increasing γ with increasing sulfuric acid concentration, starting from a concentration where formaldehyde protonation is thought to be the dominant solvation mechanism. The uptake seems to be irreversible in 10–20 ml sulfuric acid solutions.

References

[1] J. T. Jayne, S. X. Duan, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. **96**, 5452 (1992).

[2] M. A. Tolbert, J. Pfaff, I. Jayaweera, and M. J. Prather, J. Geophys. Res. **98**, 2957 (1993).

CH_3CHO + Substrate (water droplets)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$\geq 3.0 \times 10^{-2}$	droplets	267	Jayne *et al.*, 1993[1]	(a)

Comments

(a) Uptake experiment on a fast monodisperse droplet train moving axially in a flow tube and sampled by a differentially pumped quadrupole MS. The droplet diameter ranged between 80 and 240 μm and the total pressure in the flow tube was between 6 and 20 Torr N_2 with the acetaldehyde density being approximately 10^{13} molecule cm^{-3}. The droplet-acetaldehyde interaction time was between 1.8 and 21 ms. The partial pressure of water vapor in the flow tube was adjusted to result in droplets ranging from the supercooled state at 260 K to near ambient temperature at 290 K. The measured uptake coefficient γ_{obs} was time dependent both at pH =6.1 and 14 at 267 K. The uptake kinetics were found to be significantly faster than predicted from known bulk thermodynamic parameters, especially at short reaction times (2 ms). A plausible explanation would be the formation of enolate ion chemisorbed at the interface. The introduction of an additional fitting parameter into the model has the effect that the accommodation coefficient becomes insensitive to the experimental data, so that only a lower limit is presented (see Table).

References

[1] J. T. Jayne, S. X. Duan, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. **96**, 5452 (1992).

$CHBr_3$ + Substrate (water ice, H_2SO_4)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\leq 6.0 \times 10^{-5}$	H_2O ice film	200	Hanson and Ravishankara, 1993[1]	(a)
γ_0	3.0×10^{-3}	58% H_2SO_4, liquid	200		

Comments

(a) Uptake experiment in a wall coated flow tube coupled to a chemical ionization MS as a probe. On ice the reaction was found to be immeasurably slow, and thus the uptake coefficient is given as an upper limit. On 58% H_2SO_4 a reversible physical adsorption was observed with an initial uptake coefficient γ=0.003 (see above) and 0.5 s exposure time. For longer exposure times (~20 s) γ decreases to 2×10^{-4} because of a probable acid-catalyzed hydrolysis reaction.

References

[1] D. R. Hanson and A. R. Ravishankara, NATO ASI Series (17), in *The Tropospheric Chemistry of Ozone in the Polar Regions*, edited by H. Niki and K. H. Becker (Springer-Verlag, Berlin, 1993), p. 281.

Alcohols, Haloalcohols, HOC_2H_4OH + Substrate (H_2O droplets)

Uptake Coeff.	Value	Condensed Phase Chemical Species	Temp./K	Reference	Comments
γ	$(5.6 \pm 1.0) \times 10^{-2}$	methanol	273	Jayne *et al.*, 1991[1]	(a)
	$(4.8 \pm 1.0) \times 10^{-2}$	ethanol	273		
	$(2.6 \pm 1.0) \times 10^{-2}$	1-propanol	273		
	$(3.2 \pm 1.0) \times 10^{-2}$	2-propanol	273		
	$(5.2 \pm 1.0) \times 10^{-2}$	2-methyl-2-propanol	273		
	$(5.7 \pm 1.0) \times 10^{-2}$	2-chloroethanol	273		
	$(6.9 \pm 1.0) \times 10^{-2}$	2-bromoethanol	273		
	$(9.9 \pm 1.0) \times 10^{-2}$	2-iodoethanol	273		
	$(7.1 \pm 1.0) \times 10^{-2}$	ethylene glycol	273		

Comments

(a) Uptake experiment on fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase sensitive detection. The total pressure was 6–20 Torr He with densities of the title compounds of the order of 5×10^{13} molecule cm^{-3}, the droplet diameter was 110–230 μm and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H_2O corresponding to a range of 260 (supercooled state) to 291 K. The uptake coefficients were corrected for gas phase diffusion using calculated or scaled diffusion coefficients in He and H_2O vapor. An additional correction owing to limited solubility was performed for methanol, ethanol, 1- and 2-propanol and 2-methyl-2-propanol because these substances showed a time-dependent uptake coefficient. The remaining uptake coefficients were found to be time-independent. From the temperature dependence of the corrected uptake coefficient which is interpreted as mass accommodation coefficient, pairs of the thermodynamic parameters for solvation, ΔH^0_{obs} and ΔS_{obs} are obtained. The pairs address the energy barrier for the transition state from gas to solution in terms of the Gibbs free energy for the transition. ΔH^0_{obs} and ΔS_{obs} seem to be correlated and are in the range of -22.2 to -46.0 kJ mol^{-1} and -102.5 to -193.3 J $mol^{-1}K^{-1}$, respectively.

References

[1] J. T. Jayne, S. X. Duan, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. 95, 6329 (1991).

HCOOH, CH_3COOH + Substrate (H_2O droplets)

Uptake Coeff.	Value	Condensed Phase Chemical Species	Temp./K	Reference	Comments
γ	$(4.7\pm1.0)\times10^{-2}$	HCOOH	273	Jayne *et al.*, 1991[1]	(a)
	$(6.7\pm1.0)\times10^{-2}$	CH_3COOH	273		
γ	$(8.9\pm1.0)\times10^{-2}$	CH_3COOH	273	Hu *et al.*, 1993[2]	(b)

Comments

(a) Uptake experiment on fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase sensitive detection. The total pressure was 6–20 Torr He with densities of the title compounds on the order of 5×10^{13} molecule cm^{-3}, the droplet diameter was 110–230 μm and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H_2O corresponding to a range of 260 (supercooled state) to 291 K. The uptake coefficients were corrected for gas phase diffusion using calculated or scaled diffusion coefficients in He and H_2O vapor. The uptake coefficients were found to be time-independent and thus not limited by solubility. From the temperature dependence of the corrected uptake coefficient which is interpreted as mass accommodation coefficient, pairs of the thermodynamic parameters for solvation, ΔH^0_{obs} and ΔS_{obs} are obtained. The pairs address the energy barrier for the transition state from gas to solution in terms of the Gibbs free energy of the transition. ΔH^0_{obs} and ΔS_{obs} were measured as -33.1 and -33.9 kJ mol^{-1} and -146.0 and -146.0 J mol^{-1} K^{-1} for formic and acetic acid, respectively.

(b) This is a redetermination of the temperature-dependent uptake coefficient using the identical experimental technique described in comment (a). The diffusion coefficient of CH_3COOH in Ar was determined by measuring the uptake coefficient over a range of pressures (3–23 Torr). The diffusion coefficient for both CH_3COOH and H_2O in He were calculated using scaling laws based on experimental values for Ar and a data base of more than 20 compounds. ΔH^0_{obs} and ΔS_{obs} were measured to be $-(35.1\pm3.3)$ kJ $mol^{-1}$and $-(148.1\pm12.1)$ J mol^{-1} K^{-1}, respectively.

References

[1] J. T. Jayne, S. X. Duan, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. 95, 6329 (1991).
[2] J. H. Hu, J. A. Shorter, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. 97, 11037 (1993).

Haloacetic acids + Substrate (H_2O droplets)

Uptake Coeff.	Value	Condensed Phase Chemical Species	Temp./K	Reference	Comments
γ	$(1.32\pm0.20)\times10^{-1}$	CCl_3COOH	273	Hu *et al.*, 1993[1]	(a)
	$(1.35\pm0.20)\times10^{-1}$	CCl_2HCOOH	273		
	$(1.39\pm0.20)\times10^{-1}$	$CClH_2COOH$	273		
	$(1.54\pm0.20)\times10^{-1}$	$CF_2ClCOOH$	273		
	$(1.39\pm0.20)\times10^{-1}$	CF_3COOH	273		

Comments

(a) Uptake experiment on fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase sensitive detection. The total pressure was 6–20 Torr He with densities of the title compounds of the order of 5×10^{13} molecule cm^{-3}, the droplet diameter was 120–250 μm, and the contact times were in the range 1.8–15 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H_2O corresponding to a range of 260 (supercooled state) to 288 K. The uptake coefficients were corrected for gas phase diffusion using scaled diffusion coefficients for the haloacetic acids in He and H_2O vapor using measured diffusion coefficients in Ar. The uptake coefficients were found to be time-independent and thus not limited by solubility. From the temperature dependence of the corrected uptake coefficient which is interpreted as mass accommodation coefficient, pairs of the thermodynamic parameters for solvation, ΔH^0_{obs} and ΔS_{obs} were obtained. The pairs address the energy barrier for the transition state from gas to solution in terms of the Gibbs free energy of the transition. ΔH^0_{obs} and ΔS_{obs} were measured to be in the range from -18.8 to -41.4 kJ mol^{-1} and from $-84.$ to -167.3 J mol^{-1} K^{-1}.

References

[1] J. H. Hu, J. A. Shorter, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. **97**, 11037 (1993).

6. Appendix 1

Enthalpy Data*

Species	$\Delta_f H^\circ_{298}$/kJ·mol^{-1}	$\Delta_f H^\circ_0$/kJ·mol^{-1}	Reference
H	217.998		20
H_2	0	0	20
O	249.18	246.8	20
O(^{1}D)	438.9	436.6	25
O_2	0	0	20
$O_2(^1\Delta)$	94.3	94.3	25
$O_2(^1\Sigma)$	156.9	156.9	25
O_3	142.7	145.4	57
HO	39.3	39.0	30
HO_2	14.6		30
H_2O	−241.826		20
H_2O_2	−136.32	−130.04	57
N	472.68		20
N_2	0	0	20
NH	352		49
NH_2	185.4	188.4	30
NH_3	−45.94		20
NO	90.25	89.75	57
NO_2	33.2	36	57
NO_3	73.7		21
N_2O	82.05	85.50	57
N_2O_4	9.1	18.7	15
N_2O_5	11.3		15,21
HNO	99.6	102.5	15
HNO_2	−79.5	−74	57
HNO_3	−135.06	−125.27	57
HO_2NO_2	−57		47
CH	596.35		30
$CH_2(^3B_1)$	392.5		30
$CH_2(^1A_1)$	430.1		30
CH_3	146.0		30
CH_4	−74.81	−66.82	57
CN	435		15,30
HCN	135		15
HCO	41.8		17
CH_2O	−108.6	−104.7	25
CH_3O	17.6		30
CH_2OH	−9		24
CH_3OH	−201.6		19
CO	−110.53		20
NCO	159		15
COOH	−223		30
HCOOH	−378.8	−371.6	19
CH_3O_2	10.4		36
CH_3OOH	−131		15
$HOCH_2O_2$	−162.1		36
CH_3ONO	−65.3		8
CH_3ONO_2	−119.7		8
$CH_3O_2NO_2$	−44		47
CO_2	−393.51		20
C_2H	565		30
C_2H_2	228.0		19
C_2H_3	279.9		52
C_2H_4	52.2		19
C_2H_5	121.5		30
C_2H_6	−84.0		19
CH_2CN	244.8		30
CH_3CN	64.3		54
CH_2CO	−47.7		45
CH_3CO	−24.3		30
CH_2CHO	12.6		30
CH=CHOH	115		53
CH_3CHO	−165.8		19,54
C_2H_5O	−17.2		30
C_2H_4OH	−34		8
CH_3CHOH	−63.6		30
C_2H_5OH	−234.8		19,54
$(CHO)_2$	−211.9		19,54
CH_3CO_2	−207.5		30
CH_3CO_2H	−432.04		19,54
$C_2H_5O_2$	−28.7		36
CH_3OOCH_3	−125.7		19,54
$CH_3C(O)O_2$	−172		36
C_2H_5ONO	−103.8		19,54
$C_2H_5ONO_2$	−154.0		19,54
$C_2H_5O_2NO_2$	−63.2		23
CH_2=$CHCH_2$	163.6		30
C_3H_6	20.2		19,54
n-C_3H_7	97.5		30
i-C_3H_7	90.0		30
C_3H_8	−104.5		19,54
CH_3COCH_2	−23.9		30
C_2H_5CHO	−187.4		19,54
CH_3COCH_3	−217.2		19,54
C_3H_6OH	−74		8
n-C_3H_7O	−41.4		30
i-C_3H_7O	−52.3		30
i-C_3H_7OH	−272.5		19,54
CH_3COCHO	−271.1		19,54
$C_3H_5O_2$	87.9		36
i-$C_3H_7O_2$	−68.9		36
n-$C_3H_7ONO_2$	−174.1		19,54
i-$C_3H_7ONO_2$	−190.8		19,54
$CH_3C(O)O_2NO_2$	−258		12
S	277.17		20
HS	143.0		44
H_2S	−20.6		20
HSO	−4		37
SO	5.0	5.0	15
HSO_2	−222		11
SO_2	−296.81		20
$HOSO_2$	−385		38
SO_3	−395.7	−390	57
HSNO	94		10
CH_3S	124.6		44
CH_3SH	−22.9		48
CH_3SCH_2	136.8		28
CH_3SCH_3	−37.24		57
CS	272	268	7
CH_3SO	−67		14
OCS	−142	−142	57
S_2	128.60		20
CH_3SS	68		7
CH_3SSCH_3	−24.3		7
CS_2	117.2	116.6	57
$HOCS_2$	110.5		41
F	79.38		20
HF	−273.30		20
HOF	−98	−95	15
FO	109	109	8
FO_2	26.1		46
FONO	67		5
FNO_2	−108.8		47
$FONO_2$	10	18	15
CH_2F	−31.8		30

Enthalpy Data*—Continued

Species	$\Delta_f H^\circ_{298}$/kJ·mol^{-1}	$\Delta_f H^\circ_0$/kJ·mol^{-1}	Reference
CH_3F	−232.6		32
CH_3CH_2F	−263		35
HCOF		−392.5	58
FCO	−171.5	−172.1	15
F_2	0	0	20
CHF_2	−238.9		30
CH_2F_2	−453		35
CH_3CHF_2	−501		35
CF_2	−194.1		30
COF_2	−634.7	−631.6	57
CHF_3	−697.6		35
CF_3	−467.4		30
CH_2CF_3	−517.1		30
CH_3CF_3	−748.7		31
CH_2FCHF_2	−691		31
CF_3O	−655.6		6
CF_3OH	−893.3		6
CF_3OF	−785		35
CF_3O_2	−614.0		36
CF_3CO_2H	−1031		48
$CF_3O_2NO_2$	−686		23
CF_4	−933	−927	51
Cl	121.30		20
HCl	−92.31		20
HOCl	−78	−75	25,39
ClO	101.6		1
ClOO	97.5		4
OClO	95.6		26,42
sym-ClO_3	232.6		18
ClNO	51.7	53.6	15
$ClNO_2$	12.5	18.0	57
ClONO	56		47
$ClONO_2$	22.9		3
CH_2Cl	121.8		55
CH_2ClO_2	9.2		36
CH_3Cl	−82.0	−74.0	51
CHF_2Cl	−483.7		16
CH_3CHFCl	−313.4		31
CH_3CF_2Cl	−536.2		31
ClCO	−21.8		43
COFCl	−427	−423	15
CFCl	20		35
CF_2Cl	−279.1		30
CF_2ClO_2	−406.5		36
$CF_2ClO_2NO_2$	−480		33
CF_3Cl	−707.9	−702.9	16
Cl_2	0	0	20
Cl_2O	81.4	83.2	2
Cl_2O_2	127.6		42
Cl_2O_3	153		13
CCl_2	239		30
$CHCl_2$	98.3		55
$CHCl_2O_2$	1.6		36
CH_2Cl_2	−95.4	−88.5	51
$CHFCl_2$	−284.9		16
$COCl_2$	−220.1	−218.4	25
$CFCl_2$	−89.1		55
$CFCl_2O_2$	−213.7		36
$CFCl_2O_2NO_2$	−286		33
CF_2Cl_2	−493.3	−489.1	16
CH_2ClCF_2Cl	−543		35
CF_3CHCl_2	−740		35
$CF_2ClCHFCl$	−724		35
CF_2ClCF_2Cl	−925.5		31
CCl_3	71.1	69.9	27
CCl_3O_2	−11.3		36
$CCl_3O_2NO_2$	−83.7		33
$CHCl_3$	−103.3		15
C_2HCl_3	−7.8	−4.3	57
CH_3CCl_3	−144.6		31
$CFCl_3$	−284.9	−281.1	16
$CF_2ClCFCl_2$	−726.8		31
CCl_4	−95.8	−93.6	51
C_2Cl_4	−12.4	−11.9	15
Br	111.87		20
HBr	−36.29		20
HOBr	−50		40
BrO	125	133	57
BrNO	82.2	91.5	57
BrONO	103		22
$BrNO_2$	63		34
$BrONO_2$	47		47
CH_2Br	169.0		55
CH_3Br	−38.1		9
CF_3Br	−650		35
CF_2ClBr	−438		35
BrCl	14.6	22.1	15
$Br_2(g)$	30.91		20
$CHBr_2$	188		55
CF_2Br_2	−379		35
CF_2BrCF_2Br	−789.9		31
$CHBr_3$	23.8		9
I	106.76		20
HI	26.50		20
HOI	−90		29
IO	107		50
INO	121.3	124.3	56
INO_2	60.2	66.5	56
CH_2I	230.1		30
CH_3I	14.2		19
CF_3I	−589		15
$I_2(g)$	62.42		20

*Most of the thermochemical data have been taken from evaluations or reviews. In some cases, we have selected more recent experimental data, which appear to be reliable.

References

[1] S. Abramowitz and M. W. Chase, Jr., Pure Appl. Chem. **63**, 1449 (1991).

[2] R. Alqasmi, H.-D. Knauth, and D. Rohlack, Ber. Bunsenges. Phys. Chem. **82**, 217 (1978).

[3] L. C. Anderson and D. W. Fahey, J. Phys. Chem. **94**, 644 (1990).

[4] S. Baer, H. Hippler, R. Rahn, M. Siefke, N. Seitzinger, and J. Troe, J. Chem. Phys. **95**, 6463 (1991).

[5] Based on equating FO-N bond strengths in FONO and $FONO_2$.

[6] L. Batt and R. Walsh, Int. J. Chem. Kinet. **14**, 933 (1982).

[7] S. W. Benson, Chem. Rev. **78**, 23 (1978).

[8] S. W. Benson, *Thermochemical Kinetics*, 2nd ed. (Wiley, New York, 1976).

[9] J. Bickerton, M. E. Minas Da Piedade, and G. Pilcher, J. Chem. Thermodyn. **16**, 661 (1984).

[10] G. Black, R. Patrick, L. E. Jusinski, and T. G. Slanger, J. Chem. Phys. **80**, 4065 (1984).

[11] R. J. Boyd, A. Gupta, R. F. Langler, S. P. Lownie, and J. A. Pincock, Can. J. Chem. **58**, 331 (1980).

[12] I. Bridier, F. Caralp, H. Loirat, R. Lesclaux, B. Veyret, K. H. Becker, A. Reimer, and F. Zabel, J. Phys. Chem. **95**, 3594 (1991).

[13] J. B. Burkholder, R. L. Mauldin, R. J. Yokelson, S. Solomon, and A. R. Ravishankara, J. Phys. Chem. **97**, 7597 (1993).

[14] Calculated from $\Delta H_f((CH_3)_2SO)$ and the value $D(CH_3\text{-}SOCH_3) = 230$ kJ mol^{-1} estimated by Benson (Ref. 7).

[15] M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, J. Phys. Chem. Ref. Data **14**, Suppl. 1 (1985).

[16] S. S. Chen, R. C. Wilhoit, and B. J. Zwolinski, J. Phys. Chem. Ref. Data **5**, 571 (1976).

[17] M.-C. Chuang, M. F. Foltz, and C. B. Moore, J. Chem. Phys. **87**, 3855 (1987).

[18] A. J. Colussi, J. Phys. Chem. **94**, 8922 (1990).

[19] J. D. Cox, and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic, London, 1970).

[20] J. D. Cox, D. D. Wagman, and V. A. Medvedev, Eds., *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1989).

[21] H. F. Davis, B. Kim, H. S. Johnston, and Y. T. Lee, J. Phys. Chem. **97**, 2172 (1993).

[22] Derived by NASA Panel (see references in Introduction) from an estimated value of D(BrONO-O) = 305 kJ mol^{-1}, by analogy with NO_2, $HONO_2$ and CH_3ONO_2.

[23] M. J. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).

[24] S. Dóbé, M. Otting, F. Temps, H. Gg. Wagner, and H. Ziemer, Ber. Bunsenges. Phys. Chem. **97**, 877 (1993).

[25] E. S. Domalski, D. Garvin, and D. D. Wagman, Appendix 1 in R. F. Hampson and D. Garvin, Natl. Bur. Stand. (U.S.) Spec. Publ. 513 (1978).

[26] R. Flesch, E. Rühl, K. Hottmann, and H. Baumgartel, J. Phys. Chem. **97**, 837 (1993).

[27] J. W. Hudgens, R. D. Johnson, R. S. Timonen, J. A. Seetula, and D. Gutman, J. Phys. Chem. **95**, 4400 (1991).

[28] A. Jefferson, J. M. Nicovich, and P. H. Wine, J. Phys. Chem. **98**, 7128 (1994).

[29] M. E. Jenkin, K. C. Clemitshaw, and R. A. Cox, J. Chem. Soc. Faraday Trans. 2, **80**, 1633 (1984); the above value is the median of the range, −77 to −102 kJ mol^{-1}, deduced in this study.

[30] J. A. Kerr, "Strengths of Chemical Bonds," in *CRC Handbook of Chemistry and Physics,* 75th ed., edited by D. R. Lide, (CRC, Boca Raton, FL, 1994).

[31] V. P. Kolesov and T. S. Papina, Russ. Chem. Rev. **52**, 425 (1983).

[32] V. P. Kolesov, Russ. Chem. Rev. **47**, 599 (1978).

[33] D. Köppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).

[34] K. D. Kreutter, J. M. Nicovich, and P. H. Wine, J. Phys. Chem. **95**, 4020 (1991); erratum, *ibid.* **96**, 7146 (1992).

[35] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, J. Phys. Chem. Ref. Data **17**, Suppl. 1 (1988).

[36] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).

[37] E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).

[38] J. J. Margitan, J. Phys. Chem. **88**, 3314 (1984).

[39] L. T. Molina and M. J. Molina, J. Phys. Chem. **82**, 2410 (1978).

[40] P. S. Monks, L. J. Stief, M. Krauss, S. C. Kuo, and R. B. Klemm, J. Chem. Phys. **100**, 1902 (1994); M. P. McGrath and F. S. Rowland, J. Phys. Chem. **98**, 4773 (1994); above value is a rounded-off average from these two papers.

[41] T. P. Murrells, E. R. Lovejoy, and A. R. Ravishankara, J. Phys. Chem. **94**, 2381 (1990).

[42] S. L. Nickolaisen, R. R. Friedl, and S. P. Sander, J. Phys. Chem. **98**, 155 (1994).

[43] J. M. Nicovich, K. D. Kreutter, and P. H. Wine, J. Chem. Phys. **92**, 3539 (1990).

[44] J. M. Nicovich, K. D. Kreutter, C. A. van Dijk, and P. H. Wine, J. Phys. Chem. **96**, 2518 (1992).

[45] R. L. Nuttall, A. H. Laufer, and M. V. Kilday, J. Chem. Thermodyn. **3**, 167 (1971).

[46] P. Pagsberg, E. Ratajczak, A. Sillesen, and J. T. Jodkowski, Chem. Phys. Lett. **141**, 88 (1987).

[47] R. Patrick and D. M. Golden, Int. J. Chem. Kinet. **15**, 1189 (1983).

[48] J. B. Pedley, R. D. Naylor, and S. P. Kirby, *Thermochemical Data of Organic Compounds*, 2nd. ed. (Chapman and Hall, London, 1986).

[49] L. G. Piper, J. Chem. Phys. **70**, 3417 (1979).

[50] R. R. Reddy, T. V. R. Rao, and A. S. R. Reddy, Indian J. Pure Appl. Chem. **27**, 243 (1989).

[51] A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski, J. Phys. Chem. Ref. Data **3**, 117 (1974).

[52] J. J. Russell, S. M. Senkan, J. A. Seetula, and D. Gutman, J. Phys. Chem. **93**, 5184 (1989).

[53] G. P. Smith, P. W. Fairchild, and D. R. Crosley, J. Chem. Phys. **81**, 2667 (1984).

[54] Sussex-N. P. L. *Computer Analysed Thermochemical Data: Organic and Organometallic Compounds,* edited by J. B. Pedley and J. Rylance (University of Sussex, England, 1977).

[55] E. Tschuikow-Roux and S. Paddison, Int. J. Chem. Kinet. **19**, 15 (1987).

[56] H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976); H. Hippler, K. Luther, H. Teitelbaum, and J. Troe, Int. J. Chem. Kinet. **9**, 917 (1977).

[57] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, J. Phys. Chem. Ref. Data **11**, Suppl. 2 1982.

[58] Y. Zhao and J. S. Francisco, Chem. Phys. Lett. **173**, 551 (1990).