Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II

CODATA Task Group on Gas Phase Chemical Kinetics

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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 atmosphere chemistry [J. Phys. Chem. Ref. Data **9**, 295 (1980); **11**, 327 (1982)]. The work has been carried out by the authors under the auspices of the CODATA Task Group on Gas Phase Chemical Kinetics. Data sheets have been prepared for 256 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.

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

Contents

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1. Preface

This paper is the second 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] The original evaluation and the first supplement were primarily intended to furnish a kinetic data base for modeling middle atmosphere chemistry (10–55 km altitude). With the publication of the present evaluation, this data base is now sufficiently firm that a future update should not be required for about four years. During this period, we anticipate that much more quantitative kinetic and photochemical data will be published on reactions involved in tropospheric chemistry, which is now of major atmospheric interest. Consequently, we envisage that any future CODATA evaluations of atmospheric chemical reactions will include more emphasis on tropospheric chemistry.

The approach to the present supplement has been to prepare data sheets for reactions for which results have been published since December 1980, i.e., data published since Supplement I.[2] At the same time, we have widened the scope of the data base by including new data sheets for C_2, C_3, and CN-containing organic species.

It should be emphasized that in preparing the updated data sheets we have not listed all the previous data contained in the original evaluation[1] and the first supplement.[2] Consequently to obtain the overall picture and background to the preferred rate parameters, it is essential that the present supplement should be read in conjunction with our previous publications.[1,2]

The cutoff point for literature searching for this supplement was September 1983. As in our previous evaluations, however, we also include data which, at the time of our final Task Group Meeting (October 1983), was available to us in preprint form.

2. 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						
1274	$O + O_2 + M \rightarrow O_3 + M$	$6.2\times10^{-34}[O_2]$	(k_0)	±0.1	$6.2\times10^{-34}(T/300)^{-2.0}[O_2]$	200–300	$\Delta n = \pm0.5$
		$5.7\times10^{-34}[N_2]$	(k_0)	±0.1	$5.7\times10^{-34}(T/300)^{-2.8}[N_2]$	200–300	$\Delta n = \pm0.5$
		2.8×10^{-12}	(k_∞)	±0.2	2.8×10^{-12}	200–300	$\Delta n = \pm0.5$
		$F_c = 0.65$		$\Delta F_c = \pm0.1$	$F_c = \exp(-T/696)$	200–300	
1275	$O_3^* + M \rightarrow O_3 + M$	See data sheets for $O + O_2 + M \rightarrow O_3 + M$					
1276	$O + O_3 \rightarrow 2O_2$	8.0×10^{-15}		±0.08	$8.0\times10^{-12}\exp(-2060/T)$	220–400	±200
**	$O + O_3^* \rightarrow O + O_3$ $\rightarrow 2O_2$	1.5×10^{-11}		±0.5			
**	$O(^1D) + O_2 \rightarrow O(^3P) + O_2(^1\Sigma_g^+)$ $\rightarrow O(^3P) + O_2(^1\Delta_g)$ $\rightarrow O(^3P) + O_2(^3\Sigma_g^-)$	4.0×10^{-11}		±0.05	$3.2\times10^{-11}\exp(+67/T)$	200–350	±100
1277	$O(^1D) + O_3 \rightarrow O_2 + 2O(^3P)$ $\rightarrow O(^3P) + O_3$ $\rightarrow 2O_2(^1\Delta_g)$ $\rightarrow O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-)$ $\rightarrow 2O_2(^3\Sigma_g^-)$	2.4×10^{-10}		±0.05	2.4×10^{-10}	100–400	±100
1278	$O_2(^1\Delta_g) + M \rightarrow O_2(^3\Sigma_g^-) + M$	$\leqslant1.4\times10^{-19}$	$(M = N_2)$				
		1.7×10^{-18}	$(M = O_2)$	±0.3			
		5×10^{-18}	$(M = H_2O)$	±0.3			
		$\leqslant2\times10^{-20}$	$(M = CO_2)$				
**	$O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$	3.8×10^{-15}		±0.1	$5.2\times10^{-11}\exp(-2840/T)$	280–360	±500
**	$O_2(^1\Delta_g)^* + M \rightarrow O_2(^1\Delta_g) + M$	See data sheets					
1279	$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^3\Sigma_g^-) + M$	2.0×10^{-15}	$(M = N_2)$	±0.1			
		8.0×10^{-14}	$(M = O)$	±0.3			
		4.0×10^{-17}	$(M = O_2)$	±0.3			
		4.0×10^{-12}	$(M = H_2O)$	±0.3			
		4.1×10^{-13}	$(M = CO_2)$	±0.2			
1280	$O_2(^1\Sigma_g^+) + O_3 \rightarrow O + 2O_2$	1.5×10^{-11}		±0.1			
	$\rightarrow O_2(^1\Delta_g) + O_3$ $\rightarrow O_2(^3\Sigma_g^-) + O_3$	6.6×10^{-12}		±0.06			
**	$O_2(^1\Sigma_g^+)^* + O_2 \rightarrow O_2(^1\Sigma_g^+) + O_2$	See data sheets					
**	$O_2 + h\nu \rightarrow 2O$	See data sheets					
1281	$O_3 + h\nu \rightarrow O + O_2$	See data sheets					

2. 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
	HO$_x$ Reactions						
1282	$H + HO_2 \rightarrow H_2 + O_2$	6.7×10^{-12}		±0.3			
	$\rightarrow 2HO$	6.4×10^{-11}		±0.2			
	$\rightarrow H_2O + O$	3.0×10^{-12}		±0.5			
1283	$H + O_2 + M \rightarrow HO_2 + M$	$5.9\times10^{-32}[O_2]$	(k_0)	±0.1	$5.9\times10^{-32}(T/300)^{-1.0}[O_2]$	200–300	$\Delta n = \pm0.6$
		$5.9\times10^{-32}[N_2]$	(k_0)	±0.1	$5.9\times10^{-32}(T/300)^{-1.0}[N_2]$	200–300	$\Delta n = \pm0.6$
		7.5×10^{-11}	(k_∞)	±0.2	$7.5\times10^{-11}(T/300)^{0.6}$	200–300	$\Delta n = \pm0.6$
		$F_c = 0.55$		$\Delta F_c = \pm0.15$	$F_c = \exp(-T/502)$	200–300	
**	$H + O_3 \rightarrow HO + O_2$	2.8×10^{-11}		±0.2	$1.4\times10^{-10} \exp(-480/T)$	220–360	±100
**	$H + O_3 \rightarrow HO^* + O_2$	See data sheets					
1284	$O + H_2 \rightarrow HO + H$	9×10^{-18}		±0.5			
1284	$O + HO \rightarrow O_2 + H$	3.3×10^{-11}		±0.1	$2.3\times10^{-11} \exp(+110/T)$	220–500	±100
1285	$O + HO_2 \rightarrow HO + O_2$	5.7×10^{-11}		±0.1	$2.9\times10^{-11} \exp(+200/T)$	200–400	±200
1286	$O + H_2O_2 \rightarrow HO + HO_2$	1.7×10^{-15}		±0.3	$1.4\times10^{-12} \exp(-2000/T)$	250–390	±1000
1287	$O(^1D) + H_2 \rightarrow HO + H$ $\rightarrow O(^3P) + H_2$	1.1×10^{-10}		±0.1	1.1×10^{-10}	200–350	±100
1288	$O(^1D) + H_2O \rightarrow 2HO$	2.2×10^{-10}		±0.1	2.3×10^{-10}	200–350	±100
	$\rightarrow H_2 + O_2$	2.3×10^{-12}		±0.3			
	$\rightarrow O(^3P) + H_2O$	1.2×10^{-11}		±0.3			
1289	$HO + H_2 \rightarrow H_2O + H$	6.7×10^{-15}		±0.1	$7.7\times10^{-12} \exp(-2100/T)$	200–450	±200
1290	$HO + H_2(v = 1) \rightarrow H_2O + H$	8.7×10^{-13}		±0.3			
**	$HO + HO \rightarrow H_2O + O$	1.8×10^{-12}		±0.15			
1290	$HO + HO + M \rightarrow H_2O_2 + M$	$6.9\times10^{-31}[O_2]$	(k_0)	±0.5	$6.9\times10^{-31}(T/300)^{-0.8}[O_2]$	200–300	$\Delta n = ^{+2}_{-0.8}$
		$6.9\times10^{-31}[N_2]$	(k_0)	±0.5	$6.9\times10^{-31}(T/300)^{-0.8}[N_2]$	200–300	$\Delta n = ^{+2}_{-0.8}$
		3.0×10^{-11}	(k_∞)	±0.5	3.0×10^{-11}	200–300	$\Delta n = \pm0.5$
		$F_c = 0.72$		$\Delta F_c = \pm0.1$	$F_c = \exp(-T/913)$	200–300	
1291	$HO + HO_2(+M) \rightarrow H_2O + O_2(+M)$	6.6×10^{-11}	(0 Torr)	±0.2			
		1.1×10^{-10}	(760 Torr N_2)	±0.2			
1293	$HO + H_2O_2 \rightarrow H_2O + HO_2$	1.7×10^{-12}		±0.1	$2.9\times10^{-12} \exp(-160/T)$	240–460	±100
**	$HO + O_3 \rightarrow HO_2 + O_2$	6.7×10^{-14}		±0.15	$1.9\times10^{-12} \exp(-1000/T)$	220–450	±300
**	$HO^* + M \rightarrow$ products	See data sheets					
**	$HO^* + O_3 \rightarrow$ products	See data sheets					
1294	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.5×10^{-12}		±0.15	$2.2\times10^{-13} \exp(+600/T)$	230–420	±200
1294	$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$	$5.4\times10^{-32}[N_2]$		±0.15	$1.9\times10^{-33}[N_2] \exp(+980/T)$	230–420	±300
**	$HO_2 + O_3 \rightarrow HO + 2O_2$	2.0×10^{-15}		±0.2	$1.4\times10^{-14} \exp(-600/T)$	250–400	$^{+500}_{-100}$
**	$H_2O + h\nu \rightarrow HO + H$	See data sheets					
**	$H_2O_2 + h\nu \rightarrow 2HO$	See data sheets					
	NO$_x$ Reactions						
**	$N + HO \rightarrow NO + H$	4.9×10^{-11}		±0.15	$3.8\times10^{-11} \exp(+85/T)$	250–500	±100
**	$N + NO \rightarrow N_2 + O$	3.1×10^{-11}		±0.15	3.1×10^{-11}	200–400	±100
1295	$N + NO_2 \rightarrow N_2O + O$	3.0×10^{-12}		±0.2			
*	$N + O_2 \rightarrow NO + O$	8.9×10^{-17}		±0.1	$4.4\times10^{-12} \exp(-3220/T)$	280 – 333	±350
**	$N + O_2(^1\Delta) \rightarrow NO + O$	$\leqslant 1\times10^{-16}$			$\leqslant 1\times10^{-16}$	200–300	

2. 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
*	$N + O_3 \rightarrow NO + O_2$	$\leqslant 1.0\times10^{-15}$					
1296	$O + NO + M \rightarrow NO_2 + M$	$8.6\times10^{-32}[O_2]$	(k_0)	± 0.2	$8.6\times10^{-32}(T/300)^{-1.8}[O_2]$	200–300	$\Delta n = \pm 0.5$
		$1.0\times10^{-31}[N_2]$	(k_0)	± 0.1	$1.0\times10^{-31}(T/300)^{-1.6}[N_2]$	200–300	$\Delta n = \pm 0.5$
		3.0×10^{-11}	(k_∞)	± 0.2	$3.0\times10^{-11}(T/300)^{+0.3}$	300–1500	$\Delta n = \pm 0.5$
		$F_c = 0.85$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/1850)$	200–300	
*	$O + NO_2 \rightarrow NO + O_2$	9.3×10^{-12}		± 0.06	9.3×10^{-12}	230–340	$^{+0}_{-150}$
*	$O + NO_2 + M \rightarrow NO_3 + M$	$9\times10^{-32}[O_2]$	(k_0)	± 0.3	$9\times10^{-32}(T/300)^{-2.0}[O_2]$	200–400	$\Delta n = \pm 1.0$
		$9\times10^{-32}[N_2]$	(k_0)	± 0.1	$9\times10^{-32}(T/300)^{-2.0}[N_2]$	200–400	$\Delta n = \pm 1.0$
		2.2×10^{-11}	(k_∞)	± 0.1	2.2×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.8$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/1300)$	200–400	
*	$O + NO_3 \rightarrow O_2 + NO_2$	1×10^{-11}		± 0.5			
*	$O + N_2O_5 \rightarrow$ products	$\leqslant 3\times10^{-16}$			$\leqslant 3\times10^{-16}$	220–300	
**	$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	2.6×10^{-11}		± 0.1	$1.8\times10^{-11} \exp(+107/T)$	200–350	± 100
**	$O(^1D) + N_2O \rightarrow N_2 + O_2$	4.4×10^{-11}		± 0.15	4.4×10^{-11}	200–350	± 100
	$\rightarrow 2NO$	7.2×10^{-11}		± 0.15	7.2×10^{-11}	200–350	± 100
	$\rightarrow O(^3P) + N_2O$	$< 0.1\times10^{-11}$					
**	$NH_2 + HO \rightarrow NH + H_2O$	No recommendation					
	$\rightarrow NH_3 + O$	No recommendation					
**	$NH_2 + HO_2 \rightarrow$ products	3.4×10^{-11}		± 0.4			
1297	$NH_2 + NO \rightarrow$ products	1.6×10^{-11}		± 0.3	$1.6\times10^{-11}(T/298)^{-1.5}$	210–500	$\Delta n = \pm 0.5$
**	$NH_2 + NO_2 \rightarrow$ products	1.7×10^{-11}		± 0.5	$1.7\times10^{-11}(T/298)^{-2.2}$	250–500	$\Delta n = \pm 1.5$
1298	$NH_2 + O_2 \rightarrow$ products	$< 3\times10^{-18}$					
**	$NH_2 + O_3 \rightarrow$ products	1.2×10^{-13}		± 0.5	$3.4\times10^{-12} \exp(-1000/T)$	250–380	± 500
1299	$NO + O_3 \rightarrow NO_2 + O_2$	1.8×10^{-14}		± 0.08	$1.8\times10^{-12} \exp(-1370/T)$	195–304	± 200
*	$NO + NO_3 \rightarrow 2NO_2$	2×10^{-11}		± 0.5			
**	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	$3.7\times10^{-30}[O_2]$	(k_0)	± 0.3	$3.7\times10^{-30}(T/300)^{-4.1}[O_2]$	200–300	$\Delta n = \pm 1.0$
		$3.7\times10^{-30}[N_2]$	(k_0)	± 0.2	$3.7\times10^{-30}(T/300)^{-4.1}[N_2]$	200–300	$\Delta n = \pm 0.5$
		1.6×10^{-12}	(k_∞)	± 0.2	$1.6\times10^{-12}(T/300)^{+0.2}$	200–520	$\Delta n = \pm 0.5$
		$F_c = 0.34$		$\Delta F_c = \pm 0.05$	$F_c = \exp(-T/280)$	200–520	
**	$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	$1.6\times10^{-19}[O_2]$	(k_0/s^{-1})	± 0.3	$2.2\times10^{-3}(T/300)^{-4.4} \exp(-11080/T)[O_2]s^{-1}$	200–330	± 500
		$1.6\times10^{-19}[N_2]$	(k_0/s^{-1})	± 0.2	$2.2\times10^{-3}(T/300)^{-4.4} \exp(-11080/T)[N_2]s^{-1}$	200–300	± 500
		6.9×10^{-2}	(k_∞/s^{-1})	± 0.3	$9.7\times10^{14}(T/300)^{+0.1} \exp(-11080/T)s^{-1}$	200–300	± 500
		$F_c = 0.34$		$\Delta F_c = \pm 0.05$	$F_c = \exp(-T/280)$	200–300	
*	$NO_2 + O_3 \rightarrow NO_3 + O_2$	3.2×10^{-17}		± 0.06	$1.2\times10^{-13} \exp(-2450/T)$	230–360	± 150
**	$HO + NH_3 \rightarrow H_2O + NH_2$	1.6×10^{-13}		± 0.15	$3.3\times10^{-12} \exp(-900/T)$	230–450	± 200
1300	$HO + NO + M \rightarrow HONO + M$	$7.4\times10^{-31}[O_2]$	(k_0)	± 0.2	$7.4\times10^{-31}(T/300)^{-2.4}[O_2]$	200–440	$\Delta n = \pm 1.0$
		$7.4\times10^{-31}[N_2]$	(k_0)	± 0.1	$7.4\times10^{-31}(T/300)^{-2.4}[N_2]$	200–440	$\Delta n = \pm 0.5$
		1.0×10^{-11}	(k_∞)	± 0.2	1.0×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.8$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/1300)$	200–400	

2. 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
1300	$HO + NO_2 + M \rightarrow HONO_2 + M$	$2.2\times10^{-30}[O_2]$	(k_0)	±0.1	$2.2\times10^{-30}(T/300)^{-2.9}[O_2]$	200–300	$\Delta n = \pm0.5$
		$2.6\times10^{-30}[N_2]$	(k_0)	±0.1	$2.6\times10^{-30}(T/300)^{-2.9}[N_2]$	200–300	$\Delta n = \pm0.5$
		5.2×10^{-11}	(k_∞)	±0.2	5.2×10^{-11}	200–300	$\Delta n = \pm0.5$
		$F_c = 0.43$		$\Delta F_c = \pm0.1$	$F_c = \exp(-T/353)$	200–300	
1302	$HO + HONO_2 \rightarrow H_2O + NO_3$	1.3×10^{-13}		±0.1	$9.4\times10^{-15}\exp(+778/T)$	220–300	±100
1303	$HO + HO_2NO_2 \rightarrow$ products	4.6×10^{-12}		±0.2	$1.3\times10^{-12}\exp(+380/T)$	240–340	$^{+270}_{-580}$
**	$HO_2 + NO \rightarrow HO + NO_2$	8.3×10^{-12}		±0.1	$3.7\times10^{-12}\exp(+240/T)$	230–500	±100
1304	$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$	$2.1\times10^{-31}[O_2]$	(k_0)	±0.1	$2.1\times10^{-31}(T/300)^{-4.6}[O_2]$	200–300	$\Delta n = \pm1.0$
		$2.3\times10^{-31}[N_2]$	(k_0)	±0.1	$2.3\times10^{-31}(T/300)^{-4.6}[N_2]$	200–300	$\Delta n = \pm1.0$
		4.2×10^{-12}	(k_∞)	±0.2	$4.2\times10^{-12}(T/300)^{0.2}$	200–300	$\Delta n = \pm1.0$
		$F_c = 0.56$		$\Delta F_c = \pm0.1$	$F_c = \exp(-T/517)$	200–300	
**	$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$	$9.3\times10^{-21}[O_2]$	(k_0/s^{-1})	±0.3	$3.6\times10^{-6}\exp(-10\,000/T)[O_2]s^{-1}$	260–300	±500
		$1.3\times10^{-20}[N_2]$	(k_0/s^{-1})	±0.3	$5\times10^{-6}\exp(-10\,000/T)[N_2]s^{-1}$	260–300	±500
		0.23	(k_∞/s^{-1})	±0.6	$3.4\times10^{14}\exp(-10\,420/T)s^{-1}$	250–300	±500
		$F_c = 0.56$		$\Delta F_c = \pm0.1$	$F_c = \exp(-T/517)$	200–300	
**	$NO + h\nu \rightarrow$ products	See data sheets					
**	$NO_2 + h\nu \rightarrow$ products	See data sheets					
**	$NO_3 + h\nu \rightarrow$ products	See data sheets					
**	$N_2O + h\nu \rightarrow$ products	See data sheets					
**	$N_2O_5 + h\nu \rightarrow$ products	See data sheets					
**	$HONO + h\nu \rightarrow$ products	See data sheets					
**	$HONO_2 + h\nu \rightarrow$ products	See data sheets					
**	$HO_2NO_2 + h\nu \rightarrow$ products	See data sheets					
	Organic Reactions						
1305	$O + CH_3 \rightarrow HCHO + H$	1.1×10^{-10}		±0.2	1.1×10^{-10}	200–300	±200
1306	$O + CN \rightarrow CO + N(^2D)$	1.4×10^{-11}		±0.2			
	$\rightarrow CO + N(^4S)$	3.4×10^{-12}		±0.2			
1307	$O(^1D) + CH_4 \rightarrow HO + CH_3$	1.4×10^{-10}		±0.1	1.4×10^{-10}	200–300	±100
	$\rightarrow HCHO + H_2$	1.5×10^{-11}			1.5×10^{-11}	200–300	±100
1308	$HO + CH_4 \rightarrow H_2O + CH_3$	8.0×10^{-15}		±0.1	$2.4\times10^{-12}\exp(-1710/T)$	200–300	±200
1309	$HO + C_2H_2 + M \rightarrow C_2H_2OH + M$	$2\times10^{-29}[O_2]$	(k_0)	±0.5	$2\times10^{-29}(T/300)^{-1.3}[O_2]$	200–300	$\Delta n = \pm2$
		$2\times10^{-29}[N_2]$	(k_0)	±0.5	$2\times10^{-29}(T/300)^{-1.3}[N_2]$	200–300	$\Delta n = \pm2$
		7.3×10^{-13}	(k_∞)	±0.3	$6.5\times10^{-12}\exp(-650/T)$	200–300	±350
		$F_c = 0.5$		$\Delta F_c = \pm0.2$	$F_c = \exp(-T/433)$	200–300	
1310	$HO + C_2H_4 + M \rightarrow C_2H_4OH + M$	$9.5\times10^{-29}[O_2]$	(k_0)	±0.3	$9.5\times10^{-29}(T/300)^{-3.1}[O_2]$	200–300	$\Delta n = \pm2$
		$9.5\times10^{-29}[N_2]$	(k_0)	±0.3	$9.5\times10^{-29}(T/300)^{-3.1}[N_2]$	200–300	$\Delta n = \pm2$
		9×10^{-12}	(k_∞)	±0.3	9×10^{-12}	200–300	$\Delta n = \pm1$
		$F_c = 0.7$		$\Delta F_c = \pm0.2$	$F_c = \exp(-T/840)$	200–300	
1312	$HO + C_2H_6 \rightarrow H_2O + C_2H_5$	2.7×10^{-13}		±0.06	$1.9\times10^{-11}\exp(-1260/T)$	295–500	±250
1313	$HO + C_3H_6 + M \rightarrow C_3H_6OH + M$	$8\times10^{-27}[O_2]$	(k_0)	±1	$8\times10^{-27}(T/300)^{-3.5}[O_2]$	200–300	$\Delta n = \pm1$
		$8\times10^{-27}[N_2]$	(k_0)	±1	$8\times10^{-27}(T/300)^{-3.5}[N_2]$	200–300	$\Delta n = \pm1$
		3.0×10^{-11}	(k_∞)	±0.1	3.0×10^{-11}	200–300	$\Delta n = \pm1$
		$F_c = 0.5$		$\Delta F_c = \pm0.2$	$F_c = \exp(-T/433)$		

2. 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
1316	$HO + C_3H_8 \rightarrow H_2O + C_3H_7$	1.2×10^{-12}		± 0.3	$1.6\times10^{-11}\exp(-800/T)$	290–500	± 250
1317	$HO + HCN \rightarrow$ products	3×10^{-14}(1 atm)		± 0.5	$1.2\times10^{-13}\exp(-400/T)$(1 atm)	296–433	± 300
1318	$HO + CH_3CN \rightarrow H_2O + CH_2CN$	3.4×10^{-14}		± 0.3	$6.7\times10^{-13}\exp(-890/T)$	250–420	± 300
1319	$HO + CO \rightarrow H + CO_2$	1.5×10^{-13}	($\leqslant$100 Torr)	± 0.05	1.5×10^{-13}	200–300	
		$(1.5\times10^{-13})\times$	(100–760	± 0.1			
		$[1 + 0.45(P/\text{atm})]$	Torr,air)				
**	$HO + HCHO \rightarrow H_2O + HCO$ $\rightarrow H_2O + H + CO$	1.1×10^{-11}		± 0.1	1.1×10^{-11}	200–425	± 150
**	$HO + CH_3OH \rightarrow H_2O + CH_2OH$ $\rightarrow H_2O + CH_3O$	1.0×10^{-12}		± 0.1			
**	$HO + CH_3CHO \rightarrow H_2O + CH_3CO$	1.6×10^{-11}		± 0.1	$6.9\times10^{-12}\exp(+260/T)$	298–450	± 300
**	$HO + CH_3CO_3NO_2 \rightarrow$ products	$\leqslant 2\times10^{-13}$					
1320	$HO_2 + HCHO \rightarrow$ products	4.5×10^{-14}		± 0.1			
**	$HO_2 + CH_3O_2 \rightarrow O_2 + CH_3O_2H$	6.5×10^{-12}	(1 atm)	± 0.7	$7.7\times10^{-14}\exp(+1300/T)$	275–338	± 700
1321	$CH_3 + O_2 \rightarrow HCHO + HO$	$< 5\times10^{-17}$					
1321	$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	$6\times10^{-31}[O_2]$	(k_0)	± 0.3	$6\times10^{-31}(T/300)^{-2}[O_2]$	200–300	$\Delta n = \pm 1$
		$6\times10^{-31}[N_2]$	(k_0)	± 0.3	$6\times10^{-31}(T/300)^{-2}[N_2]$	200–300	$\Delta n = \pm 1$
		1.8×10^{-12}	(k_∞)	± 0.3	1.8×10^{-12}	200–300	$\Delta n = \pm 1$
		$F_c = 0.51$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/446)$		
1323	$CH_3 + O_3 \rightarrow$ products	2.6×10^{-12}		± 0.3	$5.4\times10^{-12}\exp(-220/T)$	240–400	± 200
1324	$CN + O_2 \rightarrow NCO + O$	1.4×10^{-11}		± 0.3			
	$\rightarrow CO + NO$	1.0×10^{-12}		± 0.3			
1325	$HCO + O_2 \rightarrow CO + HO_2$	5.6×10^{-12}		± 0.2	$3.5\times10^{-12}\exp(+140/T)$	300–500	± 150
**	$CH_3O + NO(+M) \rightarrow CH_3ONO(+M)$	2×10^{-11}		± 0.5	2×10^{-11}	200–400	
1326	$CH_3O + NO_2(+M) \rightarrow CH_3ONO_2(+M)$	1.2×10^{-11}		± 0.3	1.2×10^{-11}	298–400	± 200
1327	$CH_3O + O_2 \rightarrow HCHO + HO_2$	1.3×10^{-15}		± 0.7	$1.1\times10^{-13}\exp(-1310/T)$	298–630	$^{+1000}_{-500}$
**	$CH_2OH + O_2 \rightarrow HCHO + HO_2$	2×10^{-12}		± 0.5			
1327	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	7.6×10^{-12}		± 0.1	$4.2\times10^{-12}\exp(+180/T)$	240–360	± 180
**	$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2$	$2.3\times10^{-30}[O_2]$	(k_0)	± 0.2	$2.3\times10^{-30}(T/300)^{-4.0}[O_2]$	200–300	$\Delta n = \pm 2$
	$+ M$	$2.3\times10^{-30}[N_2]$	(k_0)	± 0.1	$2.3\times10^{-30}(T/300)^{-4.0}[N_2]$	200–300	$\Delta n = \pm 2$
		8×10^{-12}	(k_∞)	± 0.2	8×10^{-12}	200–300	$\Delta n = \pm 0.5$
		$F_c = 0.4$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/327)$		
**	$CH_3O_2NO_2 + M \rightarrow CH_3O_2 +$ $NO_2 + M$	No recommendation					
**	$CH_3O_2 + O_3 \rightarrow CH_3O + 2O_2$	$< 2\times10^{-17}$					
1328	$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH$ $+ HCHO + O_2$	$\geqslant 2.1\times10^{-13}$		± 0.3			
	$\rightarrow 2CH_3O + O_2$	1.3×10^{-13}		± 0.3			
	$\rightarrow CH_3OOCH_3 + O_2$	$\leqslant 3\times10^{-14}$		± 0.3			
1329	$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	2×10^{-13}		± 0.3			
1330	$C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$	$2.0\times10^{-28}[O_2]$	(k_0)	± 0.3	$2.0\times10^{-28}(T/300)^{-3.8}[O_2]$	200–300	$\Delta n = \pm 1$
		$2.0\times10^{-28}[N_2]$	(k_0)	± 0.3	$2.0\times10^{-28}(T/300)^{-3.8}[N_2]$	200–300	$\Delta n = \pm 1$
		5×10^{-12}	(k_∞)	± 0.3	5×10^{-12}	200–300	$\Delta n = \pm 1$
		$F_c = 0.7$		$\Delta F_c = \pm 0.2$	$F_c = \exp(-T/840)$		
1331	$CH_3CO + O_2(+M) \rightarrow CH_3CO_3(+M)$	2×10^{-12}	(1–4 Torr)				
		5×10^{-12}	(k_∞)	± 0.5	5×10^{-12}	200–300	$\Delta n = \pm 1$

2. 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
1332	$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	8×10^{-15}		± 0.5			
1332	$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$	$\geqslant 7.1\times10^{-12}$		± 0.3			
1332	$C_2H_5O_2 + NO + M \rightarrow C_2H_5O_2NO + M$	$\leqslant 1.8\times10^{-12}$		± 0.3			
1333	$C_2H_5O_2 + NO_2(+M) \rightarrow C_2H_5O_2NO_2(+M)$	5×10^{-12}	(k_∞)	± 0.5	5×10^{-12}	200–300	$\Delta n = \pm 1$
	$C_2H_5O_2NO_2(+M) \rightarrow C_2H_5O_2 + NO_2(+M)$	No recommendation					
1333	$C_2H_5O_2 + C_2H_5O_2 \rightarrow C_2H_5OH + CH_3CHO + O_2$	$\geqslant 3.9\times10^{-14}$		± 0.3			
	$\rightarrow 2C_2H_5O + O_2$	5.2×10^{-14}		± 0.3			
	$\rightarrow C_2H_5OOC_2H_5 + O_2$	$\leqslant 9\times10^{-15}$		± 0.3			
**	$CH_3CO_3 + NO \rightarrow CH_3 + CO_2 + NO_2$	1.4×10^{-11}		± 0.7			
**	$CH_3CO_3 + NO_2(+M) \rightarrow CH_3CO_3NO_2(+M)$	6×10^{-12}	(1 atm)	± 0.5			
**	$CH_3CO_3NO_2(+M) \rightarrow CH_3CO_3 + NO_2(+M)$	4.2×10^{-4} s^{-1}	(1 atm)	± 0.1	$1.12\times10^{16}\exp(-13330/T)$ s^{-1} (1 atm)	295–330	± 1000
1334	n-$C_3H_7 + O_2 + M \rightarrow n$-$C_3H_7O_2 + M$	6×10^{-12}	(k_∞)	± 0.3	6×10^{-12}	200–300	$\Delta n = \pm 1$
1334	i-$C_3H_7 + O_2 + M \rightarrow i$-$C_3H_7O_2 + M$	1.5×10^{-11}	(k_∞)	± 0.3	1.5×10^{-11}	200–300	$\Delta n = \pm 1$
1335	n-$C_3H_7O_2 + NO + M \rightarrow n$-$C_3H_7O_2NO + M$	2.9×10^{-13}	(k_∞)	± 0.5	2.9×10^{-13}	200–300	$\Delta n = \pm 1$
1335	i-$C_3H_7O_2 + NO_2 + M \rightarrow i$-$C_3H_7O_2NO_2 + M$	5.6×10^{-12}	(k_∞)	± 0.5	5.6×10^{-12}	200–300	$\Delta n = \pm 1$
1335	n-$C_3H_7O_2 + NO \rightarrow n$-$C_3H_7O + NO_2$	7.6×10^{-12}		± 0.5			
**	$HCHO + h\nu \rightarrow$ products	See data sheets					
**	$CH_3OOH + h\nu \rightarrow$ products	See data sheets					
**	$CH_3OONO_2 + h\nu \rightarrow$ products	See data sheets					
1336	$CH_3CHO + h\nu \rightarrow$ products	See data sheets					
**	$CH_3CO_3NO_2 + h\nu \rightarrow$ products	See data sheets					
	<u>SO_x Reactions</u>						
**	$O + H_2S \rightarrow HO + HS$	2.2×10^{-14}		± 0.3	$1.4\times10^{-11}\exp(-1920/T)$	290–500	± 750
*	$O + CS \rightarrow CO + S$	2.1×10^{-11}		± 0.1	$2.7\times10^{-10}\exp(-760/T)$	150–300	± 250
1337	$O + CH_3SCH_3 \rightarrow CH_3SO + CH_3$	5.0×10^{-11}		± 0.1	$1.3\times10^{-11}\exp(+409/T)$	270–560	± 100
1338	$\left.\begin{array}{l} O + CS_2 \rightarrow SO + CS \\ \rightarrow CO + S_2 \\ \rightarrow OCS + S \end{array}\right\}$	3.6×10^{-12}		± 0.2	$3.2\times10^{-11}\exp(-650/T)$	200–500	± 100
1339	$O + CH_3SSCH_3 \rightarrow CH_3SO + CH_3S$	1.3×10^{-10}		± 0.3	$5.5\times10^{-11}\exp(+250/T)$	290–570	± 100
*	$O + OCS \rightarrow SO + CO$	1.4×10^{-14}		± 0.2	$2.6\times10^{-11}\exp(-2250/T)$	220–600	± 150
*	$O + SO_2 + M \rightarrow SO_3 + M$	$1.4\times10^{-33}[O_2]$	(k_0)	± 0.3	$4.0\times10^{-32}\exp(-1000/T)[O_2]$	200–400	$^{+200}_{-100}$
		$1.4\times10^{-33}[N_2]$	(k_0)	± 0.3	$4.0\times10^{-32}\exp(-1000/T)[N_2]$	200–400	$^{+200}_{-100}$
**	$S + O_2 \rightarrow SO + O$	2.3×10^{-12}		± 0.2	2.3×10^{-12}	230–400	± 200

2. 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
*	$S + O_3 \rightarrow SO + O_2$	1.2×10^{-11}		± 0.3			
1340	$HO + H_2S \rightarrow H_2O + HS$	4.8×10^{-12}		± 0.08	$6.3\times10^{-12}\exp(-80/T)$	200–300	± 80
1341	$HO + CH_3SCH_3 \rightarrow$ products	7.8×10^{-12}		± 0.2			
1341	$HO + CS_2 \rightarrow$ products	$\leqslant 7.0\times10^{-15}$	$([O_2] = 0)$				
		2.0×10^{-12}	(1 atm air)	± 0.3	$8.8\times10^{-16}\exp(+2300/T)$	260–300	± 500
1342	$HO + CH_3SSCH_3 \rightarrow$ products	2.0×10^{-10}		± 0.1	$6.0\times10^{-11}\exp(+380/T)$	250–370	± 300
1343	$HO + OCS \rightarrow$ products	6×10^{-16}		± 0.3	$1.3\times10^{-12}\exp(-2300/T)$	200–520	± 250
1344	$HO + SO_2 + M \rightarrow HOSO_2 + M$	$5.0\times10^{-31}[O_2]$	(k_0)	± 0.3	$5.0\times10^{-31}(T/300)^{-3.3}[O_2]$	200–300	$\Delta n = \pm 0.5$
		$5.0\times10^{-31}[N_2]$	(k_0)	± 0.3	$5.0\times10^{-31}(T/300)^{-3.3}[N_2]$	200–300	$\Delta n = \pm 0.5$
		2×10^{-12}	(k_∞)	± 0.3	2×10^{-12}	200–300	$\Delta n = \pm 1$
		$F_c = 0.45$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/380)$	200–300	
**	$HO_2 + SO_2 \rightarrow$ products	$\leqslant 1\times10^{-18}$					
1345	$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3$	$< 5\times10^{-17}$					
	$\rightarrow CH_3O_2SO_2$	No recommendation					
1346	$HS + O_2 \rightarrow HO + SO$	$< 3.2\times10^{-15}$					
1346	$HS + NO \rightarrow$ products	5.9×10^{-13}		± 0.2			
*	$CS + O_2 \rightarrow CO + SO$	No recommendation					
	$\rightarrow OCS + O$	(see data sheets)					
1347	$SO + O_2 \rightarrow SO_2 + O$	6.7×10^{-17}		± 0.15	$1.4\times10^{-13}\exp(-2275/T)$	230–420	± 500
1348	$SO + O_3 \rightarrow SO_2 + O_2$	8.9×10^{-14}		± 0.1	$4.5\times10^{-12}\exp(-1170/T)$	230–420	± 150
1348	$SO + NO_2 \rightarrow SO_2 + NO$	1.4×10^{-11}		± 0.1			
*	$SO_3 + H_2O \rightarrow$ products	No recommendation					
		(see data sheets)					
1349	$CS_2 + h\nu \rightarrow$ products	See data sheets					
**	$CH_3SSCH_3 + h\nu \rightarrow$ products	See data sheets					
1350	$OCS + h\nu \rightarrow$ products	See data sheets					
	FO_x Reactions						
*	$O + FO \rightarrow O_2 + F$	5×10^{-11}		± 0.5			
*	$O + FO_2 \rightarrow O_2 + FO$	5×10^{-11}		± 0.7			
*	$O(^1D) + HF \rightarrow HO + F$						
	$\rightarrow O(^3P) + HF$	1×10^{-10}		± 0.5			
1351	$O(^1D) + COF_2 \rightarrow CO_2 + F_2$	2.2×10^{-11}		± 0.2			
	$\rightarrow O(^3P) + COF_2$	5.2×10^{-11}		± 0.2			
**	$F + H_2 \rightarrow HF + H$	2.8×10^{-11}		± 0.1	$1.9\times10^{-10}\exp(-570/T)$	190–770	± 150
1352	$F + O_2 + M \rightarrow FO_2 + M$	$1.3\times10^{-32}[O_2]$	(k_0)	± 0.3	$1.3\times10^{-32}(T/300)^{-1.4}[O_2]$	200–300	$\Delta n = \pm 1$
		$1.3\times10^{-32}[N_2]$	(k_0)	± 0.3	$1.3\times10^{-32}(T/300)^{-1.4}[N_2]$	200–300	$\Delta n = \pm 1$
		3×10^{-11}	(k_∞)	± 0.5	3×10^{-11}	200–300	$\Delta n = \pm 1$
		$F_c = 0.85$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/1850)$	200–300	
*	$F + O_3 \rightarrow FO + O_2$	1.3×10^{-11}		± 0.3	$2.8\times10^{-11}\exp(-226/T)$	250–365	± 200
1352	$F + H_2O \rightarrow HF + HO$	1.1×10^{-11}		± 0.5	$4.2\times10^{-11}\exp(-400/T)$	240–370	± 200
1353	$F + NO_2 + M \rightarrow FONO + M$	$1.0\times10^{-30}[O_2]$	(k_0)	± 0.5	$1.0\times10^{-30}(T/300)^{-2.0}[O_2]$	200–300	$\Delta n = \pm 1$
		$1.0\times10^{-30}[N_2]$	(k_0)	± 0.5	$1.0\times10^{-30}(T/300)^{-2.0}[N_2]$	200–300	$\Delta n = \pm 1$
		2×10^{-10}	(k_∞)	± 0.8	2×10^{-10}	200–300	$\Delta n = \pm 1$
		$F_c = 0.6$		$\Delta F_c = \pm 0.2$	$F_c = \exp(-T/587)$	200–300	
1354	$F + CH_4 \rightarrow HF + CH_3$	8×10^{-11}		± 0.2	$3.0\times10^{-10}\exp(-400/T)$	250–450	± 200
*	$FO + O_3 \rightarrow F + 2O_2$						
	$\rightarrow FO_2 + O_2$	No recommendation					

2. 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
**	$FO + NO \rightarrow F + NO_2$	2.6×10^{-11}		± 0.3			
*	$FO + NO_2 + M \rightarrow FONO_2 + M$	$1.6\times10^{-31}[O_2]$	(k_0)	± 0.7	$1.6\times10^{-31}(T/300)^{-3.4}[O_2]$	200–300	$\Delta n = \pm 1.0$
		$1.6\times10^{-31}[N_2]$	(k_0)	± 0.7	$1.6\times10^{-31}(T/300)^{-3.4}[N_2]$	200–300	$\Delta n = \pm 1.0$
		2×10^{-11}	(k_∞)	± 0.5	2×10^{-11}	200–300	$\Delta n = \pm 0.5$
		$F_c = 0.5$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/433)$	200–300	
*	$FO + FO \rightarrow 2F + O_2$ $\rightarrow FO_2 + F$ $\rightarrow F_2 + O_2$	1.5×10^{-11}		± 0.3			
**	$HF + h\nu \rightarrow$ products	See data sheets					
1355	$COF_2 + h\nu \rightarrow$ products	See data sheets					
**	$FONO_2 + h\nu \rightarrow$ products	See data sheets					
	ClO_x Reactions						
1356	$O + HCl \rightarrow HO + Cl$	1.4×10^{-15}		± 0.3	$1.0\times10^{-11}\exp(-3340/T)$	293–718	± 350
**	$O + HOCl \rightarrow HO + ClO$	6×10^{-15}		± 1.0	$1\times10^{-11}\exp(-2200/T)$	200–300	± 1000
1356	$O + ClO \rightarrow O_2 + Cl$	4.3×10^{-11}		± 0.1	$6.4\times10^{-11}\exp(-120/T)$	220–370	± 120
*	$O + ClONO_2 \rightarrow ClO + NO_3$ $\rightarrow OClO + NO_2$ $\rightarrow O_2 + ClONO$	1.9×10^{-13}		± 0.1	$3.0\times10^{-12}\exp(-808/T)$	213–295	± 200
**	$O(^1D) + CF_2Cl_2 \rightarrow ClO + CF_2Cl$ $\rightarrow O(^3P) + CF_2Cl_2$ $\rightarrow COF_2 + Cl_2$ $\rightarrow COFCl + FCl$	1.4×10^{-10}		± 0.1			
**	$O(^1D) + CFCl_3 \rightarrow ClO + CFCl_2$ $\rightarrow O(^3P) + CFCl_3$ $\rightarrow COFCl + Cl_2$ $\rightarrow COCl_2 + FCl$	2.3×10^{-10}		± 0.1			
**	$O(^1D) + CCl_4 \rightarrow ClO + CCl_3$ $\rightarrow O(^3P) + CCl_4$ $\rightarrow COCl_2 + Cl_2$	3.3×10^{-10}		± 0.1			
1357	$Cl + H_2 \rightarrow HCl + H$	1.6×10^{-14}		± 0.1	$3.7\times10^{-11}\exp(-2300/T)$	200–300	± 200
1358	$Cl + HO_2 \rightarrow HCl + O_2$	3.2×10^{-11}		± 0.2	$1.8\times10^{-11}\exp(170/T)$	250–420	± 250
1358	$Cl + HO_2 \rightarrow ClO + HO$	9.1×10^{-12}		± 0.3	$4.1\times10^{-11}\exp(-450/T)$	250–420	± 250
*	$Cl + H_2O_2 \rightarrow HCl + HO_2$	4.3×10^{-13}		± 0.2	$1.1\times10^{-11}\exp(-980/T)$	265–424	± 500
*	$Cl + O_3 \rightarrow ClO + O_2$	1.2×10^{-11}		± 0.06	$2.7\times10^{-11}\exp(-257/T)$	205–298	± 100
**	$Cl + CH_4 \rightarrow HCl + CH_3$	1.0×10^{-13}		± 0.1	$9.6\times10^{-12}\exp(-1350/T)$	200–300	± 250
*	$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	5.7×10^{-11}		± 0.06	$7.7\times10^{-11}\exp(-90/T)$	220–350	± 100
1359	$Cl + HCHO \rightarrow HCl + HCO$	7.3×10^{-11}		± 0.06	$8.2\times10^{-11}\exp(-34/T)$	200–500	± 100
1360	$Cl + HONO_2 \rightarrow HCl + NO_3$	$\leqslant 1.7\times10^{-14}$					
*	$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$	4.9×10^{-13}		± 0.1	$3.4\times10^{-11}\exp(-1260/T)$	233–350	± 200
1360	$Cl + CH_3CCl_3 \rightarrow HCl + CH_2CCl_3$	$<4\times10^{-14}$					
1361	$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$	1.2×10^{-11}		± 0.12	$6.8\times10^{-12}\exp(160/T)$	219–298	± 200
1362	$HO + HCl \rightarrow H_2O + Cl$	6.6×10^{-13}		± 0.08	$2.8\times10^{-12}\exp(-425/T)$	210–460	± 100
**	$HO + HOCl \rightarrow H_2O + ClO$	1.8×10^{-12}		± 1.0	$3\times10^{-12}\exp(-150/T)$	200–300	$^{+850}_{-150}$

2. 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
1362	$HO + ClO \rightarrow HO_2 + Cl$ $\rightarrow HCl + O_2$	1.2×10^{-11}		± 0.2	$9.2\times10^{-12} \exp(66/T)$	250–335	± 200
*	$HO + ClONO_2 \rightarrow HOCl + NO_3$ $\rightarrow HO_2 + ClONO$ $\rightarrow HNO_3 + ClO$	3.9×10^{-13}		± 0.2	$1.2\times10^{-12} \exp(-330/T)$	246–387	± 200
**	$HO + CH_3Cl \rightarrow H_2O + CH_2Cl$	4.2×10^{-14}		± 0.1	$1.9\times10^{-12} \exp(-1120/T)$	247–350	± 200
**	$HO + CH_2FCl \rightarrow H_2O + CHFCl$	4.4×10^{-14}		± 0.1	$2.6\times10^{-12} \exp(-1210/T)$	245–350	± 100
**	$HO + CHF_2Cl \rightarrow H_2O + CF_2Cl$	4.7×10^{-15}		± 0.1	$1.1\times10^{-12} \exp(-1620/T)$	250–360	± 100
**	$HO + CHFCl_2 \rightarrow H_2O + CFCl_2$	3.0×10^{-14}		± 0.1	$1.1\times10^{-12} \exp(-1070/T)$	240–350	± 100
**	$HO + C_2HCl_3 \rightarrow$ products	2.2×10^{-12}		± 0.1	$5.0\times10^{-13} \exp(+445/T)$	234–420	± 445
**	$HO + C_2Cl_4 \rightarrow$ products	1.7×10^{-13}		± 0.1	$9.4\times10^{-12} \exp(-1200/T)$	297–420	± 200
*	$HO + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$	1.2×10^{-14}		± 0.15	$5.1\times10^{-12} \exp(-1800/T)$	250–460	± 200
**	$ClO + HO_2 \rightarrow HOCl + O_2$ $\rightarrow HCl + O_3$ $ClO + HO_2 + (M) \rightarrow HOOClO + (M)$	5.0×10^{-12}		± 0.15	$4.6\times10^{-13} \exp(+710/T)$	235–298	$^{+250}_{-700}$
**	$ClO + H_2CO \rightarrow$ products	$< 10^{-15}$					
1363	$ClO + O_2(^1\Delta) \rightarrow$ sym ClO_3	$\leqslant 3\times10^{-15}$					
**	$ClO + NO \rightarrow Cl + NO_2$	1.7×10^{-11}		± 0.1	$6.2\times10^{-12} \exp(+294/T)$	202–415	± 100
1364	$ClO + NO_2 + M \rightarrow ClONO_2 + M$	$1.7\times10^{-31}[O_2]$	(k_0)	± 0.1	$1.7\times10^{-31}(T/300)^{-3.4}[O_2]$	200–300	$\Delta n = \pm 1.0$
		$1.7\times10^{-31}[N_2]$	(k_0)	± 0.1	$1.7\times10^{-31}(T/300)^{-3.4}[N_2]$	200–300	$\Delta n = \pm 1.0$
		2×10^{-11}	(k_∞)	± 0.3	2×10^{-11}	200–300	$\Delta n = \pm 0.5$
		$F_c = 0.5$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/430)$		
1365	$HOCl + h\nu \rightarrow$ products	See data sheets					
**	$COFCl + h\nu \rightarrow$ products	See data sheets					
1366	$ClONO_2 + h\nu \rightarrow$ products	See data sheets					
**	$COCl_2 + h\nu \rightarrow$ products	See data sheets					
**	$CF_2Cl_2 + h\nu \rightarrow$ products	See data sheets					
**	$CFCl_3 + h\nu \rightarrow$ products	See data sheets					
**	$CCl_4 + h\nu \rightarrow$ products	See data sheets					
	BrO_x Reactions						
1367	$O + HBr \rightarrow HO + Br$	3.7×10^{-14}		± 0.12	$6.6\times10^{-12} \exp(-1540/T)$	220–455	± 200
1367	$O + Br_2 \rightarrow BrO + Br$	1.4×10^{-11}		± 0.2			
*	$O + BrO \rightarrow O_2 + Br$	3×10^{-11}		± 0.5			
**	$Br + HO_2 \rightarrow HBr + O_2$	No recommendation (see data sheets)					
**	$Br + H_2O_2 \rightarrow HBr + HO_2$	$\leqslant 2\times10^{-15}$					
1368	$Br + H_2CO \rightarrow HBr + HCO$	1.0×10^{-12}		± 0.15	$1.7\times10^{-11} \exp(-800/T)$	223–480	± 250
*	$Br + O_3 \rightarrow BrO + O_2$	1.1×10^{-12}		± 0.1	$1.4\times10^{-11} \exp(-760/T)$	220–360	± 200
1369	$HO + HBr \rightarrow H_2O + Br$	8.0×10^{-12}		± 0.2	8.0×10^{-12}	249–416	± 250
1369	$HO + Br_2 \rightarrow HOBr + Br$	4.2×10^{-11}		± 0.3			
*	$HO + CH_3Br \rightarrow H_2O + CH_2Br$	3.8×10^{-14}		± 0.1	$7.6\times10^{-13} \exp(-890/T)$	244–350	± 200
1370	$BrO + HO_2 \rightarrow HOBr + O_2$ $\rightarrow HBr + O_3$	5×10^{-12}		± 0.5			
*	$BrO + NO \rightarrow Br + NO_2$	2.1×10^{-11}		± 0.1	$8.7\times10^{-12} \exp(+260/T)$	224–425	± 100

2. 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
**	$BrO + NO_2 + M \rightarrow BrONO_2 + M$	$5.0\times10^{-31}[O_2]$	(k_0)	± 0.3	$5.0\times10^{-31}(T/300)^{-3.0}[N_2]$	200–300	$\Delta n = \pm 1$
		$5.0\times10^{-31}[N_2]$	(k_0)	± 0.3	$5.0\times10^{-31}(T/300)^{-3.0}[N_2]$	200–300	$\Delta n = \pm 1$
		2×10^{-11}	(k_∞)	± 0.3	2×10^{-11}	200–300	$\Delta n = \pm 0.5$
		$F_c = 0.4$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/327)$	200–300	
*	$BrO + O_3 \rightarrow Br + 2O_2$	$<5\times10^{-15}$		$^{+0.5}_{-?}$			
*	$BrO + ClO \rightarrow Br + OClO$	6.7×10^{-12}		± 0.3			
	$\rightarrow Br + Cl + O_2$ $\rightarrow BrCl + O_2$	6.7×10^{-12}		± 0.3			
1371	$BrO + BrO \rightarrow 2Br + O_2$	2.2×10^{-12}		± 0.1	$1.1\times10^{-12}\exp(+255/T)$	223–398	± 300
	$\rightarrow Br_2 + O_2$	4.5×10^{-13}		± 0.2			
1372	$BrO + h\nu \rightarrow$ products	See data sheets					
**	$HOBr + h\nu \rightarrow$ products	See data sheets					
**	$BrONO_2 + h\nu \rightarrow$ products	See data sheets					
	IO_x Reactions						
1373	$O + I_2 \rightarrow IO + I$	1.4×10^{-10}		± 0.3	1.4×10^{-10}	200–400	± 250
**	$O + IO \rightarrow O_2 + I$	5×10^{-11}		± 0.5			
**	$HO + HI \rightarrow H_2O + I$	1.3×10^{-11}		± 0.5			
**	$I + HO_2 \rightarrow HI + O_2$	No recommendation					
**	$I + O_3 \rightarrow IO + O_2$	1.0×10^{-12}		± 1.0			
**	$I + NO + M \rightarrow INO + M$	$1.8\times10^{-32}[O_2]$	(k_0)	± 0.2	$1.8\times10^{-32}(T/300)^{-1.0}[O_2]$	200–300	$\Delta n = \pm 0.5$
		$1.8\times10^{-32}[N_2]$	(k_0)	± 0.1	$1.8\times10^{-32}(T/300)^{-1.0}[N_2]$	200–300	$\Delta n = \pm 0.5$
		1.7×10^{-11}	(k_∞)	± 0.3	1.7×10^{-11}	200–300	$\Delta n = \pm 0.5$
		$F_c = 0.75$		$\Delta F_c = \pm 0.15$	$F_c = \exp(-T/1043)$		
**	$I + NO_2 + M \rightarrow INO_2 + M$	$2.9\times10^{-31}[O_2]$	(k_0)	± 0.3	$2.9\times10^{-31}(T/300)^{-1.0}[O_2]$	200–300	$\Delta n = \pm 0.5$
		$2.9\times10^{-31}[N_2]$	(k_0)	± 0.3	$2.9\times10^{-31}(T/300)^{-1.0}[N_2]$	200–300	$\Delta n = \pm 0.5$
		6.6×10^{-11}	(k_∞)	± 0.3	6.6×10^{-11}	200–300	$\Delta n = \pm 0.5$
		$F_c = 0.63$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/650)$		
**	$IO + HO_2 \rightarrow$ products	No recommendations					
**	$IO + NO \rightarrow I + NO_2$	1.7×10^{-11}		± 0.3			
1373	$IO + NO_2 + M \rightarrow IONO_2 + M$	$3.4\times10^{-31}[O_2]$	(k_0)	± 0.5	$3.4\times10^{-31}(T/300)^{-3.0}[O_2]$	200–400	$\Delta n = \pm 1$
		$3.4\times10^{-31}[N_2]$	(k_0)	± 0.5	$3.4\times10^{-31}(T/300)^{-3.0}[N_2]$	200–400	$\Delta n = \pm 1$
		1.6×10^{-11}	(k_∞)	± 0.5	1.6×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.4$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/327)$		
1374	$IO + IO \rightarrow 2I + O_2$ $\rightarrow I_2 + O_2$	No recommendation					
**	$INO + INO \rightarrow I_2 + 2NO$	1.3×10^{-14}		± 0.4	$8.4\times10^{-11}\exp(-2620/T)$	298–450	± 600
**	$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$	4.7×10^{-15}		± 0.5	$2.9\times10^{-11}\exp(-2600/T)$	298–400	± 1000
1375	$IO + h\nu \rightarrow$ products	See data sheets					
**	$HOI + h\nu \rightarrow$ products	See data sheets					
**	$INO + h\nu \rightarrow$ products	See data sheets					
**	$INO_2 + h\nu \rightarrow$ products	See data sheets					
**	$IONO_2 + h\nu \rightarrow$ products	See data sheets					

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*Data sheet for this reaction appears in earlier evaluation, J. Phys. Chem. Ref. Data **9**, 295 (1980)

Data sheet for this reaction appears in earlier evaluation, J. Phys. Chem. Ref. Data **11, 327 (1982).

3. Guide to the Data Sheets

The data sheets are of two types: (i) those for the thermal reactions and (ii) those for the photochemical reactions.

3.1. 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 I.

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 here only data which have been published since the previous CODATA evaluations,[1,2] and under heading (iii) are listed the preferred rate data from the most recent NASA evaluations,[3,4] from our own CODATA evaluation,[2] and from any new review or evaluation sources. 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, $k = A \exp(-C/T)$, where $C = E/R$. For a few bimolecular reactions, we have listed temperature dependences in the alternative form, $k = A'T^{-n}$, 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 subsequent section of the introduction.

Single temperature data are presented as such and wherever possible the rate coefficient at 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. For measurements of relative rate coefficients, 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 is that 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 the 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.

3.2. 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.,

$$A + A \rightarrow B + C,$$

$$-(\tfrac{1}{2})d[A]/dt = d[B]/dt = d[C]/dt = k[A]^2.$$

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 $2k[A]^2$) and as a power on the right-hand side.

3.3. Treatment of Combination and Dissociation Reactions

The rates of combination and the reverse dissociation reactions

$$A + B + M \rightleftarrows AB + M,$$

depend on the temperature T, the nature, and the 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

$$\frac{d[AB]}{dt} = k[A][B],$$

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

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

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

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

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

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

where the "center of the falloff curve" $[M]_c$ indicates the third body concentration for which the extrapolated k_0 would be equal to k_∞. This is illustrated in Fig. 1. 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 sim-

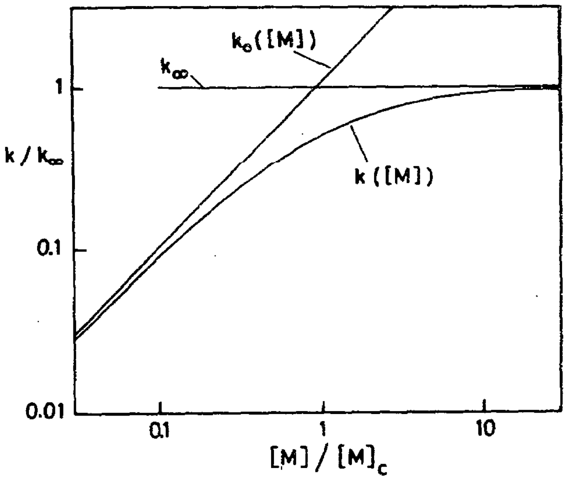

FIG. 1. Reduced falloff curve of k/k_∞ as a function of $[\mathrm{M}]/[\mathrm{M}]_c$.

ple approximate relationship holds:

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty} F = k_0 \left(\frac{1}{1 + [\mathrm{M}]/[\mathrm{M}]_c} \right) F$$
$$= k_\infty \left(\frac{[\mathrm{M}]/[\mathrm{M}]_c}{1 + [\mathrm{M}]/[\mathrm{M}]_c} \right) F,$$

where the first factors at the rhs represent the Lindemann–Hirshelwood expression, and the additional broadening factor F is approximately given by

$$\log F \cong \frac{\log F_c}{1 + [\log([\mathrm{M}]/[\mathrm{M}]_c)]^2}.$$

In this way the three quantities, k_0, k_∞, and F_c with

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

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.[5–7] The results can usually be represented[7] 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. 1, for simplicity $a = 1$ and $T^{**} \simeq 4T^{*}$ was adopted. If F_c values are available for one temperature only, we also follow this policy in the present evaluation. Often the term $\exp(-T^{**}/T)$ is negligible at temperatures below 300 K. More detailed representations, however, will require specification of a, T^{***}, T^{*}, and T^{**}. Theoretical predictions of F_c[5–7] have been derived from rigid RRKM-type models including weak collision effects. Systematic calculations of this type have been presented by Patrick and Golden[8] for reactions of atmospheric interest. It is debatable whether these calculations can be applied to radical recombination reactions without barriers, where rotational effects are important. Changes in F_c would require changes in the limiting k_0 and k_∞ values. For the purposes 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.

The dependence of k_0 and k_∞ on the temperature T is represented in the T exponent n

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

(except for the cases with an established energy barrier in the potential). We have used this form of temperature dependence because it 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 analogously to the combination reactions with pseudo-first-order rate constants k ([M]). The rate constants expressed in units of second^{-1} are denoted in the tables by the symbols (k_0/s^{-1}) and $(k_\infty/\mathrm{s}^{-1})$.

3.4. 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 calculated from the data in Appendix I. Calculated threshold wavelengths corresponding to these enthalpy changes are also listed.

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 wavelength intervals of 5 nm where possible. The preferred data are often amplified by diagrams of absorption cross sections versus wavelength and, where appropriate, by diagrams of quantum yield versus wavelength.

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

This evaluation contains data sheets only for photochemical reactions for which new data have been published since December 1980. Consequently for many of the photochemical reactions listed in the Summary of Reactions, it is necessary to refer back to our previous evaluations[1,2] for the corresponding detailed data sheets.

3.5. 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 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 1 standard atmosphere and temperature of 273 K (expressed in cm^{-1}), multiply the value of σ in cm^2 by 2.69×10^{19}. For other conversion factors, see Appendix II.

3.6. 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 $E/R = H \pm G$.

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 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.

We do not feel justified now in assigning error limits to the parameters reported for the photochemical reactions.

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The Chairman and members of the Task Group wish to express their appreciation to CODATA for the substantial financial help which greatly facilitated and accelerated the preparation of this report. In addition we thank the World Meterological Organization for additional financial assistance in organizing our meetings.

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4. Data Sheets

4.1. Oxygen Compounds

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

$\Delta H^\circ = -106.5$ 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			
$(5.96 \pm 0.34) \times 10^{-34} (T/300)^{-2.37 \pm 0.37} [O_2]$	227–353	Lin and Leu, 1982[1]	(a)
$(5.70 \pm 0.19) \times 10^{-34} (T/300)^{-2.62 \pm 0.18} [N_2]$	218–366		
$(3.81 \pm 0.28) \times 10^{-34} (T/300)^{-2.54 \pm 0.40} [Ar]$	220–353		
Reviews and Evaluations			
$6.9 \times 10^{-34} (T/300)^{-1.25} [O_2]$	200–370	CODATA, 1982[2]	(b)
$6.2 \times 10^{-34} (T/300)^{-2.0} [N_2]$			
$3.9 \times 10^{-34} (T/300)^{-1.9} [Ar]$			
$6.0 \times 10^{-34} (T/300)^{-2.3} [air]$	200–300	NASA, 1982[3]	(c)
$6.0 \times 10^{-34} (T/300)^{-2.3} [air]$	200–300	NASA, 1983[4]	(c)

Comments

(a) O_3 flash photolysis–O resonance fluorescence technique. Apparent activation energies for $M = O_2$, N_2, and Ar equal within experimental error $[E/R = (-689 \pm 17)$ K]. This result disagrees with the earlier result by Klais, Anderson, and Kurylo.[5] Relative efficiencies of M, N_2: O_2: Ar: He = 1.0: 0.99: 0.69: 0.60 at 298 K.

(b) Based on data by Klais, Anderson, and Kurylo.[5]

(c) Average of data by Lin and Leu[1] and Klais, Anderson, and Kurylo.[5]

Preferred Values

$k_0 = 6.2 \times 10^{-34} (T/300)^{-2.0} [O_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

$k_0 = 5.7 \times 10^{-34} (T/300)^{-2.8} [N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

Our previous recommendation[2] was based on the data from Klais, Anderson, and Kurylo.[5] The new data from Lin and Leu[1] indicate a much smaller difference in the temperature coefficients for $M = O_2$ and N_2. The recommended value is the average of Refs. 1, 5, and Arnold and Comes.[6] It should be noted that the unusually strong temperature dependence can have various sources such as unusually inefficient energy transfer properties, adiabatic zero point energy barriers,[7] or a major contribution from the radical-complex mechanism in addition to the energy-transfer mechanism.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.8 \pm 1) \times 10^{-12}$	295	Croce-Cobos and Troe, 1984[9]	(a)
Reviews and Evaluations			
2.8×10^{-12}	295	CODATA, 1982[2]	(b)

Comments

(a) O_2 laser flash photolysis at 193 nm in the presence of high pressures of N_2. O_3 formation followed by time-resolved uv absorption. Measurements up to 200 atm of N_2 allow to follow the falloff curve of recombination up to $[N_2]_c$.

(b) Based on earlier relative rate measurements of $k(O + O_2)/k(O + NO_2)$.

Preferred Value

$k_\infty = 2.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over range 200–300 K.

Comments on Preferred Value

The new direct measurement agrees with earlier indirect determinations.

Intermediate Falloff Range

From the preferred values one derives $[N_2]_c = 5 \times 10^{21}$ molecule cm^{-3} at 298 K. The extrapolated k_∞ value[9] is based on a broadening factor of $F_c = 0.65^8$ (300 K). For 220 K, $F_c = 0.73$ was estimated. These values agree with $F_c \simeq \exp(-T/T^*)$ where $T^* = 696$ K.

Vibrational deactivation of O_3^* formed by combination $O + O_2 \rightarrow O_3^*$

$$O + O_2 \rightarrow O_3^{**} \qquad (1)$$

$$O_3^{**} + M \rightarrow O_3(1,0,0), O_3(0,0,1) + M \qquad (2)$$

$$O_3(1,0,0), O_3(0,0,1) + M \rightarrow O_3(0,1,0) + M \qquad (3)$$

$$O_3(0,1,0) + M \rightarrow O_3(0,0,0) + M \qquad (4)$$

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	M	Temp./K	Reference	Comments
Absolute Rate Coefficients				
$k_3 = 9.8 \times 10^{-15}$	O_2	300	Joens, Burkholder, and Bair, 1982[10]	(a)
$k_3 = 4.6 \times 10^{-15}$	Ar			
$k_3 = 2.3 \times 10^{-14}$	O_2	300	Adler-Golden and Steinfeld, 1980[11]	(b)
$k_4 = 2.4 \times 10^{-14}$	O_2	300	Joens, Burkholder, and Bair, 1982[10]	(a)
$k_4 = 9.5 \times 10^{-15}$	Ar			
$k_4 = 7.0 \times 10^{-14}$	O_2	300	Adler-Golden and Steinfeld, 1980[11]	(b)
Reviews and Evaluations				
$k_2 = 3 \times 10^{-12}$	O_2	300	CODATA, 1982	(c)

Comments

(a) Flash photolysis of O_2; time-resolved observation of transient uv absorption spectra of O_3 and kinetic modeling based on a three-step model involving reactions (1), (2), (3), and (4). Analysis based on the assumption that changes of the uv spectrum are dominated by bimodal spectral contributions from the $O_3(1,0,0)$ state [and higher $O_3(n,0,0)$ states]. A theoretical confirmation of this assumption was given by Sheppard and Walker.[12]

(b) CO_2 laser excitation of O_3. Observation of transient uv absorption spectra of O_3, see also Adler-Golden, Schweitzer, and Steinfeld, 1982.[13] The given data have been reevaluated in Ref. 10.

(c) Based on evaluation of collision efficiencies in recombination of O_3 from Troe, 1979.

Preferred Values

$k_2 = 3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for $M = O_2$ at 298 K.

$k_3 = 1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for $M = O_2$ at 298 K.

$k_4 = 2.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for $M = O_2$ at 298 K.

Reliability

$\Delta \log k_2 = \pm 0.5$.
$\Delta \log k_3 = \pm 0.3$.
$\Delta \log k_4 = \pm 0.3$.

Comments on Preferred Values

k_2 unchanged from CODATA, 1982.[2] k_3 and k_4 are from the analysis by Joens, Burkholder, and Bair, 1982.[10]

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$O + O_3 \rightarrow 2O_2$

$\Delta H^\circ = -391.9$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.6 \pm 2.1)\times10^{-12}\exp[-(1950 \pm 110)/T]$	237–377	Wine *et al.*, 1983[1]	(a)
8.26×10^{-15}	297		
Reviews and Evaluations			
$1.5\times10^{-11}\exp(-2218/T)$	200–300	NASA, 1982[2]	(b)
$1.8\times10^{-11}\exp(-2300/T)$	220–400	CODATA, 1982[5]	(c)
$8.0\times10^{-12}\exp(-2060/T)$	200–300	NASA, 1983[8]	(d)

Comments

(a) $O(^3P)$ produced by laser photolysis of O_3 at 532 nm. [O] monitored by time-resolved resonance fluorescence.

(b) Based on McCrumb and Kaufman,[3] Davis *et al.*[4]

(c) Based on citations in (b) plus West *et al.*,[6] Arnold and Comes.[7]

(d) Unweighted least-squares fit to data cited in (b), (c), and Wine *et al.*[1]

Preferred Values

$k = 8.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.0\times10^{-12}\exp(-2060/T)$cm^3 molecule^{-1} s^{-1} over range 220–400 K.

Reliability

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

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

Comments on Preferred Values

The recent 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 that of McCrumb and Kaufman,[3] Davis *et al.*,[4] West *et al.*,[6] and Arnold and Comes.[7]

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

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

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.5 \pm 0.2)\times 10^{-10}$	298	Greenblatt and Wiesenfeld, 1983[1]	(a)
Branching Ratios			
$k_1/k = 0.53$ $k_5/k = 0.47$	298	Cobos, Castellano, and Schumacher, 1983[2]	(b)
Reviews and Evaluations			
2.4×10^{-10}	200–300	NASA, 1982[3]	(c)
$k_1/k = k_5/k = 0.5$	298		
2.4×10^{-10}	100–400	CODATA, 1982[9]	(c)
$k_1/k = k_5/k \approx 0.5$	298		
2.4×10^{-10}	200–300	NASA, 1983[10]	(c)
$k_1/k = k_5/k = 0.5$	298		

Comments

(a) Laser photolysis of O_3 at 248 and 308 nm. Flow system, $[O(^3P)]$ monitored by time-resolved resonance fluorescence.

(b) Steady-state photolysis of pure O_3 and O_3/inert gas mixtures. Ozone removal monitored manometrically at high pressures and spectrophotometrically at lower pressures. Quantum yield of O_3 interpreted in terms of complex reaction scheme.

(c) Based on Streit *et al.*,[4] Amimoto *et al.*,[5,6] Ravishankara and Wine,[7] Davenport *et al.*[8]

Preferred Values

$k = 2.4\times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 100–400 K.

$k_1/k = k_5/k = 0.5$ at 298 K.

Reliability

$\Delta \log k = \pm 0.05$ over range 100–400 K.

$\Delta \log k_1/k = \Delta \log k_5/k = \pm 0.1$ at 298 K.

Comments on Preferred Values

The recent measurement of k by Greenblatt and Wiesenfeld[1] is in excellent agreement with our previous recommendation. The determination of k_1/k_5 by Cobos *et al.*[2] is rather indirect but provides further evidence that $k_1 \approx k_5$. Our previous recommendations are unchanged.

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

$\Delta H^\circ = -94.3$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	M	Temp./K	Reference	Comments
Absolute Rate Coefficients				
$(1.51 \pm 0.05) \times 10^{-18}$	O_2	298	Borrell, Borrell, and Pedley, 1977[1]	(a)
$(1.47 \pm 0.05) \times 10^{-18}$	O_2	298	Leiss *et al.*, 1978[2]	(b)
$(3.0 \pm 0.4) \times 10^{-18}$	O_2	298	McLaren, Morris, and Wayne, 1981[3]	(c)
$(2.56 \pm 0.12) \times 10^{-18}$	CO_2	298	Yaron, von Engel, and Vidaud, 1976[4]	(d)
$(6-13) \times 10^{-21}$	CO_2	298	Leiss *et al.*, 1978[2]	(b)
$\leqslant 3.6 \times 10^{-19}$	CO_2	298	McLaren, Morris, and Wayne, 1981[3]	(c)
Reviews and Evaluations				
2.2×10^{-18}	O_2	298	CODATA, 1982[5]	(e)
$\leqslant 1.4 \times 10^{-19}$	N_2			(f)
5×10^{-18}	H_2O			(g)
$\leqslant 8 \times 10^{-20}$	CO_2			(g)

Comments

(a) Discharge-flow system. $O_2(^1\Delta_g)$ generated by microwave discharge in O_2 saturated with Hg, O atoms removed with Ag wool. $[O_2(^1\Delta_g)]$ monitored by dimol emission at 634 nm or by emission at 762 nm from $O_2(^1\Sigma_g^+)$.

(b) $O_2(^1\Delta_g)$ produced by microwave discharge in O_2, O atoms removed using Ag wool, products passed into a large (220 m^3) static reactor at low pressures (< 500 mTorr). $[O_2(^1\Delta_g)]$ monitored by emission at 1.27 μm using a germanium detector.

(c) $O_2(^1\Delta_g)$ produced by microwave discharge in O_2 in fast-flow system. $[O_2(^1\Delta_g)]$ monitored by emission at 1.27 μm using a germanium detector.

(d) Discharge-flow system $O_2(^1\Delta_g)$ produced by microwave discharge in O_2, AgO used to remove O atoms. $[O_2(^1\Delta_g)]$ monitored by isothermal calorimetry.

(e) Based on Findlay and Snelling.[8]

(f) Based on Hampson *et al.*,[6] Collins *et al.*[7]

(g) Based on Findlay and Snelling,[8] Becker *et al.*[9]

Preferred Values

$k = 1.7 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} for $M = O_2$ at 298 K.

$k \leqslant 1.4 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} for $M = N_2$ at 298 K.

$k = 5 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} for $M = H_2O$ at 298 K.

$k \leqslant 2 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} for $M = CO_2$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ for $M = O_2$ and $M = H_2O$.

Comments on Preferred Values

In their earliest measurements, Wayne *et al.*[10] used an energy sensitive detector to monitor $[O_2(^1\Delta_g)]$ which, they suggest, may have led to their erroneously high value of $k(M = CO_2)$. In their more recent study,[3] using a different detection method, a much lower limit of $k(M = CO_2)$ was obtained, compatible with values from other laboratories. The results of Yaron *et al.*[4] are also suspect because of the detection method used. The new results of Leiss *et al.*[2] using a more sensitive detector than in the earlier work of this group brings their upper limit for $k(M = CO_2)$ down to 1.3×10^{-20} cm^3 molecule^{-1} s^{-1} which is close to that of Findlay and Snelling.[8] We base our revised recommendation on these two studies.[2,8]

For $k(M = O_2)$ the best recent measurement[1,2] are in accord with the previous work of Findlay and Snelling,[8] Leiss *et al.*,[2] and Borrell *et al.*[1]

Our previous recommendations for $k(M = H_2O)$ and $k(M = N_2)$ are unchanged.

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

$\Delta H^\circ = -156.9$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	M	Temp./K	Reference	Comments
Absolute Rate Coefficients				
$(1.7^{+1.3}_{-0.6})\times10^{-15}\exp[(48\pm120)/T]$	N_2	203–349	Kohse-Hoinghaus and Stuhl, 1980[1]	(a)
$(2.1\pm0.6)\times10^{-15}$		298		
2.0×10^{-13}	CO_2	298	Stuhl and Welge, 1969[2]	(b)
4.4×10^{-13}	CO_2	298	Filseth, Zia, and Welge, 1970[3]	(b)
$(3.0\pm0.5)\times10^{-13}$	CO_2	298	Noxon, 1970[4]	(c)
1.5×10^{-13}	CO_2	298	O'Brien and Myers, 1970[5]	(d)
$(4.1\pm0.3)\times10^{-13}$	CO_2	298	Davidson, Kear, and Abrahamson, 1972[6]	(e)
$(4.53\pm0.29)\times10^{-13}$	CO_2	298	Aviles, Muller, and Houston, 1980[7]	(f)
$(5.0\pm0.3)\times10^{-13}$	CO_2	298	Muller and Houston, 1981[8]	(g)
$(3.4\pm0.4)\times10^{-13}$	CO_2	298	Borrell, Borrell, and Grant, 1983[9]	(h)
Relative Rate Coefficients				
2.7×10^{-13}	CO_2	298	Becker, Groth, and	(i)
2.4×10^{-13}	CO_2	298	Schurath, 1971[10]	(j)
8.0×10^{-14}	CO_2	298		(k)
Reviews and Evaluations				
4.0×10^{-17}	O_2	298	CODATA, 1982[11]	(l)
2.0×10^{-15}	N_2			(m)
8.0×10^{-14}	O			(n)
4.0×10^{-12}	H_2O			(o)

Comments

(a) $O_2(^1\Sigma_g^+)$ produced by laser photolysis of O_2. Time-resolved emission of $O_2(^1\Sigma_g^+)$ at 762 nm monitored.

(b) Vacuum uv pulsed photolysis of O_2. Time-resolved emission of $O_2(^1\Sigma_g^+)$ at 762 nm monitored.

(c) Vacuum uv photolysis of O_2 to give $O(^1D)$. $O_2(^1\Sigma_g^+)$ produced by energy transfer from $O(^1D)$. Time-resolved emission of $O_2(^1\Sigma_g^+)$ at 760 nm monitored.

(d) Discharge-flow study. $O_2(^1\Delta_g)$ produced by microwave discharge in O_2. $O_2(^1\Sigma_g^+)$ produced by $2O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-) + O_2(^1\Sigma_g^+)$. $O_2(^1\Sigma_g^+)$ selectively removed by aluminium surface. Growth of $O_2(^1\Sigma_g^+)$ back to steady state monitored by observation of emission at 762 nm.

(e) Flash photolysis of SO_2/O_2 mixtures. $O_2(^1\Sigma_g^+)$ produced by energy transfer from SO_2. Time-resolved emission from $O_2(^1\Sigma_g^+)$ at 760 nm followed.

(f) Direct excitation of $O_2(^1\Sigma_g^+)$ $(v^1 = 0)$ by Raman shifted dye laser. Time-resolved emission from $O_2(^1\Sigma_g^+)$ at 760 nm followed.

(g) Pulsed laser dissociation of O_3 in O_2/CO_2 mixtures. Decay of $O_2(^1\Sigma_g^+)$ fluorescence at 760 nm followed and the appearance of $CO_2(\nu_3)$ fluorescence.

(h) Discharge-flow study. $O_2(^1\Sigma_g^+)$ produced by microwave discharge in O_2 containing traces of Hg. $[O_2(^1\Sigma_g^-)]$ monitored using emission at 762 nm. Measurements carried out for CO_2 and N_2O at 293 K and over range 600–1300 K. For both quenchers, the value of k increases slightly to a maximum value and then declines with increasing temperature in a non-Arrhenius fashion.

(i) $O_2(^1\Delta_g)$ from microwave discharge passed into static reactor. Steady-state concentration of $O_2(^1\Sigma_g^+)$, produced by energy pooling reaction of $O_2(^1\Delta_g)$, monitored at 262 nm. $k/k\,[O_2(^1\Sigma_g^+) + N_2] = 1.36\times10^2$ obtained from which k calculated using $k\,[O_2(^1\Sigma_g^+) + N_2] = 2.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

(j) Method as in (i) $k/k\,[O_2(^1\Sigma_g^+) + H_2O] = 6\times10^{-2}$ cm^3 molecule^{-1} s^{-1} obtained from which k calculated using $k\,[O_2(^1\Sigma_g^+) + H_2O] = 4.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

(k) Method as in (i). $k/k\,[O_2(^1\Sigma_g^+) + O_2] = 2\times10^3$ cm^3 molecule^{-1} s^{-1} obtained from which k calculated using $k\,[O_2(^1\Sigma_g^+) + O_2] = 4.0\times10^{-17}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

(l) Based on Thomas and Thrush,[12] Martin *et al.*,[13] Lawton *et al.*,[14] Chatha *et al.*[15]

(m) Based on Martin *et al.*,[13] Chatha *et al.*[15]

(n) Value of Slanger and Black.[16]

(o) Value of Thomas and Thrush.[12]

Preferred Values

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

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

$k = 8.0\times10^{-14}$ cm^3 molecule^{-1} s^{-1} for $M = O$ 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 $M = CO_2$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ for $M = O_2$, O, H_2O at 298 K.

$\Delta \log k = \pm 0.2$ for $M = CO_2$ at 298 K.

$\Delta \log k = \pm 0.1$ for $M = N_2$ at 298 K.

$\Delta (E/R) = \pm 200$ K for $M = N_2$.

Comments on Preferred Values

The value of k ($M = N_2$) obtained by Kohse-Hoinghaus and Stuhl[1] is in excellent agreement with our previous recommendation and provides the only measurements of this rate coefficient over a temperature range.

The measured values of k ($M = CO_2$), which were not considered in our previous evaluation, are generally in good agreement, the exceptions being the earlier results of Stuhl and Welge[2] which were superseded by their later work,[3] the work of O'Brien and Myers[5] in which the technique was probably at fault, and the relative measurements of Becker *et al.*[10] where low values are obtained particularly when k ($M = O_2$) is used as the reference rate constant. Our recommendation is the mean of the remaining six studies.[3,4,6–9]

The recommendations for k ($M = N_2$, O_2, O, H_2O) are unchanged from our previous evaluation.[11]

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

$\Delta H^\circ(1) = -50.4$ 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
Relative Rate Coefficients			
$(1.8 \pm 0.3)\times10^{-11}$	298	Ogren *et al.*, 1982[1]	(a)
Reviews and Evaluations			
2.2×10^{-11}	298	CODATA, 1982[2]	(b)

Comments

(a) Flash photolysis of O_3/O_2 mixtures (100 Torr total pressure). $[O_3]$ monitored by absorption at 265 nm. Rate constant obtained by computer fit to proposed reaction scheme.

(b) Based on Gilpin *et al.*,[3] Snelling,[4] Slanger and Black,[5] and Amimoto and Wiesenfeld.[6]

Preferred Values

$k = 2.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 1.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

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

Comments on Preferred Values

The recent study of Ogren *et al.*[1] is in good agreement with our previous recommendations which are therefore unchanged.

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$O_3 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_0/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Sigma_g^-)$	(1)	101.4	1180
$\rightarrow O(^3P) + O_2(a^1\Delta_g)$	(2)	195.7	611
$\rightarrow O(^3P) + O_2(b^1\Sigma_g^+)$	(3)	258.3	463
$\rightarrow O(^1D) + O_2(^3\Sigma_g^-)$	(4)	291.2	411
$\rightarrow O(^1D) + O_2(a^1\Delta_g)$	(5)	385.5	310
$\rightarrow O(^1D) + O_2(b^1\Sigma_g^+)$	(6)	448.1	267

Absorption cross-section data

Wavelength range/nm	Reference	Comments
310–320	Podolske and Johnston, 1983[1]	(a)

Quantum yield data

Quantum yields	Wavelength/nm	Reference	Comments
$\phi(O^3P) = 0.093 \pm 0.028$ $\phi(O^1D) = 0.907 \pm 0.028$	248	Wine and Ravishankara, 1982[2]	(b)
$\phi(O^1D) = 0.92 \pm 0.04$	253.7	Cobos, Castellano, and Schumacher, 1983[3]	(c)
$\phi(O^1D) = 0.94 \pm 0.01$	248	Greenblatt and Wiesenfeld, 1983[5]	(d)
$\phi(O^1D) = 0.79 \pm 0.02$	308		

Comments

(a) Measured at 298 K at 0.1 nm intervals over range. Resolution 0.167 nm.

(b) Laser flash-photolysis of O_3 at 248 nm. $O(^3P)$ detected by resonance fluorescence. $O(^3P)$ yields from $O(^1D)$ deactivation by H_2O, N_2O, CH_4, and H_2 found to be 0.049 ± 0.032, < 0.040, < 0.043, and < 0.049, respectively.

(c) Steady-state photolysis of pure O_3. Ozone removal measured manometrically at high pressures and spectrophotometrically at low O_3 concentrations. Ferrioxalate actinometry used.

(d) Laser photolysis of O_3 at 248 and 308 nm. Flow system, $[O(^3P)]$ monitored by time-resolved resonance fluorescence.

Preferred Values

Unchanged from CODATA 1982.[4]

Comments on Preferred Values

The absorption cross-section data of Podolske and Johnston[1] are only 2%–10% lower throughout the range 310–320 nm than those previously recommended which in this range were based on Moortgat and Warneck.[6]

The recent quantum yield measurements of Cobos *et al.*,[3] Greenblatt and Wiesenfeld,[5] and of Wine and Ravishankara[2] are in agreement, within experimental error, with our previous recommendations.

References

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4.2. Hydrogen Compounds

$$\mathrm{H + HO_2 \rightarrow H_2 + O_2} \quad (1)$$
$$\mathrm{\rightarrow 2HO} \quad (2)$$
$$\mathrm{\rightarrow H_2O + O} \quad (3)$$

$\Delta H^\circ(1) = -220$ kJ mol^{-1}
$\Delta H^\circ(2) = -142$ kJ mol^{-1}
$\Delta H^\circ(3) = -213$ 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			
$(7.4 \pm 1.2)\times 10^{-11}$	296	Sridharan, Qiu, and Kaufman, 1982[1]	(a)
Relative Rate Coefficients			
$k_2 = 3.3\times 10^{-11}$	349	Pagsberg, Eriksen, and Christensen, 1979[2]	(b)
$(5.0 \pm 1.3)\times 10^{-11}$	298	Thrush and Wilkinson, 1981[3]	(c)
Branching Ratios			
$k_2/k = 0.87 \pm 0.04$ $k_3/k = 0.04 \pm 0.02$	296 296	Sridharan, Qiu, and Kaufman, 1982[1]	(a)
Reviews and Evaluations			
4.7×10^{-11}	298	CODATA, 1982[4]	(d)
7.4×10^{-11}	200–300	NASA, 1983[6]	(e)

Comments

(a) Discharge-flow system. HO_2 produced by reaction of F with H_2O_2. $[HO_2]$ monitored by conversion to HO by reaction with NO and laser resonance fluorescence detection of HO. [H] and [O] monitored by resonance fluorescence.

(b) Pulse radiolysis of NH_3/O_2 mixtures. Steady-state concentration of HO measured as a function of $[NH_3]/[O_2]$. Extensive reaction scheme used to model system and hence derive k_2 by fit of results to computed [HO]. Results not claimed to be highly accurate.

(c) Discharge-flow system. Laser magnetic resonance measurement of steady-state concentration of HO_2 produced by the reactions $H + O_2 + M \rightarrow HO_2 + M$ and $H + HO_2 \rightarrow$ products, where M = Ar/O_2 mixtures. Value of k derived from measurements of $k(H + O_2 + M)[O_2][M]$ using $k(H + O_2 + Ar) = 1.8\times 10^{-32}$ cm^6 molecule^{-2} s^{-1} and assuming $k(H + O_2 + O_2)/k(H + O_2 + Ar) = 3$.

(d) Accepts the value of Hack *et al.*[5]

(e) Accepts value of Sridharan *et al.*[1]

Preferred Values

$k = 7.4\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 6.7\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 6.4\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_3 = 3.0\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta \log k_1 = \pm 0.3$ at 298 K.
$\Delta \log k_2 = \pm 0.2$ at 298 K.
$\Delta \log k_3 = \pm 0.5$ at 298 K.

Comments on Preferred Values

The study of Sridharan, Qiu, and Kaufman[1] in which several species were monitored is the most careful and comprehensive to date. Their findings are preferred to those from other studies[3,4] in which slightly lower values of k were obtained. In the work of Pagsberg *et al.*[2] at 349 K the method used was indirect and until further confirmatory studies are carried out we make no recommendation for the temperature coefficient of k_2. If the results of Pagsberg *et al.*[2] are correct, a small negative temperature coefficient is implied.

References

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

$\Delta H^\circ = -207.6$ 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			
$6.0\times10^{-32}[H_2]$	298	Nielsen *et al.*, 1982[1]	(a)
$6.5\times10^{-32}[N_2]$	298	Cobos, Hippler, and Troe, 1984[2]	(b)
Reviews and Evaluations			
$5.9\times10^{-32}(T/300)^{-1.0}[N_2]$	200–400	CODATA, 1980[3]	(c)
$5.5\times10^{-32}(T/300)^{-1.4}$[air]	200–300	NASA, 1982[4]	(c)
$5.5\times10^{-32}(T/300)^{-1.6}$[air]	200–300	NASA, 1983[5]	(c),(d)

Comments

(a) Pulse radiolysis of 1 atm H_2 in presence of 0.6–38 Torr of O_2. Detection of HO_2 formation by uv absorption at 230 nm.

(b) Laser flash photolysis at 193 nm of NH_3 in presence of O_2 and M. Detection of HO_2 formation by uv absorption at 230 nm. Relative efficiencies of M, N_2: Ar: CH_4 = 1.0: 0.43: 2.3. Calculated temperature coefficients for N_2 give $n = 0.5$ over range 200–400 K.

(c) Based on data by Kurylo[6] and Wong and Davis[7].

(d) Temperature coefficient slightly changed following the calculation by Patrick and Golden.[8]

Preferred Value

$k_0 = 5.9\times10^{-32}(T/300)^{-1.0}[N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 0.6$.

Comments on Preferred Value

The new data agree well with the earlier recommendation. The markedly different relative efficiencies N_2: Ar have been confirmed. The temperature coefficient adopted here is an average of the NASA evaluation[4,8] and the calculations in Ref. 2.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
7.5×10^{-11}	298	Cobos, Hippler, and Troe, 1984[2]	(a)

Comments

(a) See comment (b) to k_0. Measurements in N_2, Ar, and CH_4 up to 200 atm. Extrapolation to the high-pressure limit using F_c given below. Calculations based on theory by Troe, 1981[6] give k_∞ (200 K)/k_∞ (300 K) = 0.81.

Preferred Value

$k_\infty = 7.5\times10^{-11}(T/300)^{0.6}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

$\Delta n = \pm 0.6$.

Comments on Preferred Value

Measurements in M = Ar, N_2, and CH_4 all extrapolate well to the same limit.

Intermediate Falloff Range

From the preferred values one derives $[N_2]_c = 1.3\times10^{21}$ molecules cm^{-3} at 298 K. The broadening factor $F_c = 0.55 \pm 0.15$ for M = N_2 from the experiments[2] agrees with the calculated value of $F_c = 0.66$ within the uncertainties. Representation of the measured value by $F_c \simeq \exp(-T/T^*)$ gives $T^* = 498$ K.

References

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$O + H_2 \rightarrow HO + H$

$\Delta H^\circ = 7.8$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$10^{-31.7 \pm 2.0} T^{6.4 \pm 0.6} \exp[(-300 \pm 300)/T]$	293–1160	Basevich and Kogarko, 1980[1]	(a)
5.0×10^{-17}	298*		
$(9.1 \pm 5.0) \times 10^{-18}$	298	Light and Matsumoto, 1980[2]	(b)
Reviews and Evaluations			
$1.6 \times 10^{-11} \exp(-4570/T)$	298–830	CODATA, 1982[3]	(c)

Comments

(a) Discharge-flow study; O produced by discharge in Ar/O_2 mixture. ESR detection of O, H, HO. Rate determined by following [O] in excess H_2; $[H_2]/[O] \geqslant 25$. Kinetics assumed to be first order and stoichiometry of 2 assumed. Arrhenius plot curved at $T < 400$ K.

(b) Discharge-flow study. $O(^3P)$ produced by reaction of N with NO. Production of $HO(v = 0)$ and $HO(v = 1)$ measured by laser resonance fluorescence. Effects of vibrational excitation of H_2 on observed k checked by experiments in which $[H_2(v = 1)]/[H_2(v = 0)]$ varied. Results suggest that presence of $H_2(v = 1)$ could not be cause of any significant departure of k from Arrhenius form for $T < 400$ K.

(c) Accepts value of Dubinsky and McKenney.[4]

Preferred Value

$k = 9 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Value

While the results of Basevich and Kogarko[1] are of doubtful value in absolute terms because of the assumptions in both their technique and data analysis, the relative values may be significant and tend to support curvature of the Arrhenius plot at $T < 400$ K. The recent study of Light and Matsumoto[2] is more direct and soundly based. Their value of k obtained at 298 K can only be reconciled with results of others at higher temperatures if a curved Arrhenius plot is involved.

For our recommendation, we accept the value of Light and Matsumoto[2] at 298 K but assign very wide error limits. We do not consider that there are enough reliable data to characterize the temperature dependence of k in the region of 298 K.

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$O + HO \rightarrow O_2 + H$

$\Delta H^\circ = -70.2$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coeficients			
$(3.1 \pm 0.5) \times 10^{-11}$	300	Brune, Schwab, and Anderson, 1983[1]	(a)
Relative Rate Coefficients			
3.3×10^{-11}	299	Keyser, 1983[2]	(b)
Reviews and Evaluations			
$2.2 \times 10^{-11} \exp(117/T)$	200–300	NASA, 1982[3]	(c)
$2.3 \times 10^{-11} \exp(110/T)$	220–500	CODATA, 1982[4]	(d)
$2.2 \times 10^{-11} \exp(117/T)$	200–300	NASA, 1983[5]	(e)

Comments

(a) Fast-flow discharge study with O atoms in excess. [HO] monitored by laser magnetic resonance and resonance fluorescence, [O] monitored by resonance fluorescence and absorption, and [H] by resonance fluorescence.

(b) Fast-flow discharge study. HO and HO_2 produced by reaction of H with NO_2 and O_2, respectively. Steady-state concentration of HO and HO_2 established in presence of excess O by reaction sequence $O + HO_2 \rightarrow HO + O_2$, $O + HO \rightarrow H + O_2$, $H + O_2 + M \rightarrow HO_2 + M$. [HO] monitored by resonance fluorescence. $[HO_2]$ determined by titration with NO and detection of HO. Measured $[HO]/[HO_2]$ gives $k/k(O + HO_2) = 0.59 \pm 0.7$. k calculated using $k(O + HO_2) = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (CODATA value).

(c) Based on Westenberg *et al.*,[4] Lewis and Watson,[5] Howard and Smith.[6]

(d) Based on Lewis and Watson,[5] Howard and Smith.[6]

(e) Based on work cited in (c) plus Keyser.[2]

Preferred Values

$k = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.3 \times 10^{-11} \exp(110/T)$ cm^3 molecule^{-1} s^{-1} over range 220–500 K.

Reliability

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

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

Comments on Preferred Values

The recent very careful study of Brune *et al.*[1] is in excellent agreement with our previous recommendations as is the relative measurement of Keyser.[2] The preferred values are unchanged from our previous evaluation.[7]

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$O + HO_2 \rightarrow HO + O_2$

$\Delta H^\circ = -220.7$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.1 \pm 0.3) \times 10^{-11} \exp[(200 \pm 28)/T]$	229–372	Keyser, 1982[1]	(a)
$(6.1 \pm 0.4) \times 10^{-11}$	299		
$(5.4 \pm 0.9) \times 10^{-11}$	296	Sridharan, Qiu, and Kaufman, 1982[2]	(b)
$(6.2 \pm 1.1) \times 10^{-11}$	298	Ravishankara, Wine, and Nicovich, 1983[3]	(c)
$(5.2 \pm 0.8) \times 10^{-11}$	300	Brune, Schwab, and Anderson, 1983[4]	(d)
Relative Rate Coefficients			
5.6×10^{-11}	299	Keyser, 1983[5]	(e)
Reviews and Evaluations			
$3.0 \times 10^{-11} \exp(200/T)$	200–300	NASA, 1982[6]	(f)
3.7×10^{-11}	298	CODATA, 1982[7]	(g)
$3.0 \times 10^{-11} \exp(200/T)$	200–300	NASA, 1983[9]	(h)

Comments

(a) Discharge-flow, resonance fluorescence technique; pseudo-first-order conditions. $[HO_2]/[O]$ in range 5–46. HO_2 generated by reaction of F atoms with H_2O_2, or reaction of Cl with CH_3OH/O_2 mixtures. O generated by discharge in He/O_2 mixtures or by pyrolysis of O_3. Values of k independent of source of species. Several potential sources of error in technique and analysis checked and small corrections made where necessary.

(b) Discharge-flow system HO_2 produced by reaction of F atoms with H_2O_2. $[HO_2]$ monitored by conversion to HO by reaction with NO and laser resonance fluorescence detection of HO. [O] monitored by resonance fluorescence.

(c) Flash-photolysis study. $O(^3P)$ produced by laser photolysis at 248 nm of O_3 in presence of large excess of N_2 to quench $O(^1D)$ rapidly to $O(^3P)$. HO_2 produced by photolysis of H_2O_2 by the laser flash. $[O(^3P)]$ monitored by time-resolved resonance fluorescence; $[HO_2]$ calculated from experimental conditions used. k independent of N_2 pressure over range 10–500 Torr and unaffected by traces (1.5 Torr) of H_2O.

(d) Fast-flow discharge study. HO and HO_2 produced by reaction of H with NO_2 and O_2, respectively. Steady-state concentration of HO and HO_2 established in presence of excess O by reaction sequence $O + HO_2 \rightarrow HO + O_2$, $O + HO \rightarrow H + O_2$, $H + O_2 + M \rightarrow HO_2 + M$. [HO] monitored by resonance fluorescence at 308 nm. $[HO_2]$ determined by titration with NO and detection of HO. Measured $[HO]/[HO_2]$ gives $k/k(O + HO) = 1.7 \pm 0.2$. k calculated using $k(O + HO) = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (CODATA value).

(e) Discharge-flow study. Experiments performed both with O atoms in excess and with HO_2 in excess. $[HO_2]$ monitored by laser magnetic resonance and by detection of HO produced from $HO_2 + NO$ reaction. [HO] monitored by laser magnetic resonance and resonance fluorescence, [O] by resonance fluorescence and absorption, [H] by resonance fluorescence.

(f) Based on Keyser[1] and Sridharan *et al.*[2]

(g) Takes average of three different measurements by Hack *et al.*[8]

(h) Based on Keyser,[1,4] Sridharan *et al.*,[2] and Ravishankara *et al.*[3]

Preferred Values

$k = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.9 \times 10^{-11} \exp(200/T)$ cm^3 molecule^{-1}s^{-1} over range 200–400 K.

Reliability

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

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

Comments on Preferred Values

The recent absolute rate coefficient measurements by Keyser,[1] Sridharan *et al.*,[2] Ravishankara *et al.*,[3] and Brune *et al.*[4] and the less precise relative measurement of Keyser[5] are all in good agreement. Previous work on this reaction has been by techniques inherently insensitive or affected by inadequate knowledge of side reactions in the system, as reflected in the wide error limits given in our previous evaluation.[6] For our present recommendation at 298 K we take a mean of the results of the four recent absolute measurements[1-4] and accept the temperature coefficient of Keyser.[1]

To obtain the tabulated value of k from the relative rate constant measurement of Keyser,[4] we have used the CODATA value of $k(O + HO)$ for the reference reaction. The fact that the value of k so obtained agrees well with the absolute measurements[1-4] of k provides further evidence of the validity of the CODATA value for $k(O + HO)$.

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$O + H_2O_2 \rightarrow HO + HO_2$

$\Delta H^\circ = -63.4$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
See comment (a)	302–349	Roscoe, 1982[1]	(a)
$(1.13 \pm 0.54) \times 10^{-12} \exp[-(2000 \pm 160)/T]$	298–386	Wine *et al.*, 1983[3]	(b)
$(1.45 \pm 0.29) \times 10^{-15}$	298		
Reviews and Evaluations			
$1.0 \times 10^{-11} \exp(-2500/T)$	200–300	NASA, 1982[4]	(c)
$1.0 \times 10^{-11} \exp(-2500/T)$	250–370	CODATA, 1982[5]	(c)
$1.4 \times 10^{-12} \exp(-2000/T)$	200–300	NASA, 1983[6]	(d)

Comments

(a) Fast-flow discharge system. O atoms produced from N + NO. [O] monitored by chemiluminescent reaction with NO. [H_2O_2] determined by trapping and titrating with $KMnO_4$. k for O removal found to vary with initial [H_2O_2]/[O_2] ratio in range 5–220. Importance of secondary reactions confirmed by computer modeling of system. Author concludes that secondary reactions affected all previous measurements except that of Davis *et al.*[2] Modeling confirms the predominance of channel leading to HO + HO_2 over the alternative giving $H_2O + O_2$.

(b) Laser flash photolysis of O_3 at 532 nm in presence of excess H_2O_2. [$O(^3P)$] monitored by time-resolved resonance fluorescence.

(c) Based on value of k at 298 K from Davis *et al.*[2] and estimated preexponential factor.

(d) Based on Davis *et al.*[2] and Wine *et al.*[3]

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 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 measurements of Roscoe[1] are of little value in deciding on the rate parameters for this reaction but do support our previous conclusion that until then the results of Davis *et al.*[2] had been the best available. The results of Wine *et al.*[3] agree with those of Davis *et al.*[2] with regard to the temperature coefficient but the absolute values of k in the two studies differ by approximately a factor of 2 throughout the range. In both cases[2,3] the preexponential factor found is low compared with other atom–molecule reactions. This has caused us previously[3] to recommend an estimated preexponential factor but in view of the care taken in the work of Wine *et al.*[3] and its reasonable agreement with the work of Davis *et al.*[2] we now recommend values based on a fit to these[2,3] two sets of data.

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

$\Delta H^\circ(1) = -181.4$ kJ mol^{-1}
$\Delta H^\circ(2) = -189.2$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.0 \pm 0.1) \times 10^{-10}$	298	Force and Wiesenfeld, 1981[1]	(a)
Relative Rate Constants			
$(7.9 \pm 0.6) \times 10^{-11}$	298	Ogren *et al.*, 1982[2]	(b)
Branching Ratios			
$k_2/k < 0.049$	298	Wine and Ravishankara, 1982[3]	(c)
Reviews and Evaluations			
1.0×10^{-10}	200–300	NASA, 1982[4]	(d)
1.1×10^{-10}	200–350	CODATA, 1982[8]	(e)
1.0×10^{-10}	200–300	NASA, 1983[9]	(d)

Comments

(a) Pulsed laser photolysis of O_3 at 248 nm. [H] and [$O(^3P)$] monitored by time-resolved absorption spectroscopy.

(b) Photolysis of O_3/H_2 mixtures in the Hartley band. $k/k[O(^1D) + O_2] = 1.97 \pm 0.15$ found from measurements of O_2 depletion. k calculated using $k[O(^1D) + O_2] = 4.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation). Reaction of $O(^1D)$ assumed to occur entirely via channel 1.

(c) Laser flash photolysis of O_3 at 248 nm. [$O(^3P)$] monitored by time-resolved resonance fluorescence.

(d) Based on Wine and Ravishankara,[3,5] Davidson *et al.*,[6,7] Force and Wiesenfeld.[1]

(e) Based on Wine and Ravishankara,[5] Davidson *et al.*[6,7]

Preferred Value

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

Reliability

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

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

Comments on Preferred Value

The recent direct measurement of k is in good agreement with our previous recommendation which is therefore unchanged. Channel 1 appears to be the predominant pathway ($> 95\%$)[3] for the reaction.

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

$\Delta H^\circ(1) = -118.7$ kJ mol^{-1}
$\Delta H^\circ(2) = -196.6$ kJ mol^{-1}
$\Delta H^\circ(3) = -189.2$ 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			
$k_1 = (2.02 \pm 0.41) \times 10^{-10}$	298	Gericke and Comes, 1981[1]	(a)
Branching Ratios			
$k_3/k = 0.049 \pm 0.032$	298	Wine and Ravishankara, 1982[2]	(b)
Reviews and Evaluations			
2.2×10^{-10}	200–300	NASA, 1982[3]	(c)
2.3×10^{-10}	200–350	CODATA, 1982[8]	(d)
2.2×10^{-10}	200–300	NASA, 1983[9]	(e)

Comments

(a) Laser flash photolysis of O_3–H_2O–Ar mixtures at 266 nm. [HO] followed by light absorption using tunable dye laser. k shown to be independent of translational energy of $O(^1D)$.

(b) Laser flash photolysis of O_3 at 248 nm. [$O(^3P)$] monitored by time-resolved resonance fluorescence.

(c) Based on Gericke and Comes,[1] Amimoto *et al.*,[4] Lee and Slanger,[5] Wine and Ravishankara,[6] Streit *et al.*[7]

(d) Based on studies cited in (c) less Gericke and Comes.[1]

(e) Based on studies cited in (c) plus Wine and Ravishankara.[2]

Preferred Values

$k = 2.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 200–350 K.

$k_1 = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 2.3 \times 10^{-12}$ 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.

$\Delta \log k_1 = \pm 0.1$, $\Delta \log k_2 = \Delta \log k_3 = \pm 0.3$ at 298 K.

Comments on Preferred Values

The recent measurement of Gericke and Comes[1] is in excellent agreement with our previous recommendations which are unchanged for k. We make use of the determination of k_3/k of Wine and Ravishankara and the earlier work of Zellner *et al.*[10] in our recommendations for the branching ratios.

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$HO + H_2 \rightarrow H_2O + H$

$\Delta H^\circ = -62.8$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.1 \pm 1.0) \times 10^{-15}$	298	Zellner and Steinert, 1981[1]	(a)
Relative Rate Coefficients			
$(8.5 \pm 1.8) \times 10^{-15}$	296	Sworski, Hochanadel, and Ogren, 1980[2]	(b)
Reviews and Evaluations			
$6.1 \times 10^{-12} \exp(-2030/T)$	200–300	NASA, 1982[3]	(c)
$7.7 \times 10^{-12} \exp(-2100/T)$	200–450	CODATA, 1982[12]	(d)
$6.1 \times 10^{-12} \exp(-2030/T)$	200–300	NASA, 1983[13]	(c)

Comments

(a) Fast flow-discharge study. $H + NO_2$ used as HO source. [HO] monitored by resonance fluorescence.

(b) Flash photolysis of H_2O–CH_4–H_2 mixtures at a total pressure of 760 Torr. [CH_3] monitored by absorption at 216 nm. k derived by computer fit of [CH_3] decay profile to assumed reaction mechanism.

(c) Based on Zellner and Steinert,[1] Greiner,[4] Tully and Ravishankara,[5] Ravishankara *et al.*,[6] Stuhl and Niki,[7] Westenberg and de Haas,[8] Smith and Zellner,[9] Overend *et al.*,[10] Atkinson *et al.*[11]

(d) Based on studies cited in (c) less Zellner and Steinert.[1]

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 range 200–450 K.

Reliability

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

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

Comments on Preferred Values

The recent measurements[1,2] yield values of k agreeing, within the error limits, with our previously recommended values, which are therefore unchanged.

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$HO + H_2(v = 1) \rightarrow H_2O + H$

$\Delta H^\circ = -115.5$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.5 \pm 3) \times 10^{-13}$	298	Zellner and Steinert, 1981[1]	(a)
$(9.9 \pm 2.4) \times 10^{-13}$	296	Glass and Chaturvedi, 1981[2]	(b)

Comments

(a) Fast flow-discharge study. H + NO_2 as HO source, $H_2(v = 1)$ produced by passing H_2 over heated filament. [HO] monitored by resonance fluorescence. $[H_2(v = 1)]$ determined by vuv absorption in the rotational lines of the (1,1) band of the $B^1\Sigma_u^+ - X^1\Sigma_g^+$ H_2 Lyman transition around 115 nm. In some experiments, chemiluminescence of HCl resulting from energy transfer was also used to determine $[H_2(v = 1)]$.

(b) Fast flow-discharge study. H + NO_2 used as HO source, $H_2(v = 1)$ produced by discharge in H_2. [HO] monitored by ESR $[H_2(v = 1)]$ determined by reacting $H_2(v = 1)$ with excess of D atoms and ESR measurement of the H atoms produced.

Preferred Value

$k = 8.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The only two studies of this reaction[1,2] use slightly different techniques but give values of k in agreement within the quoted error limits. The recommended value of k is the mean of the two. The vibrational excitation of H_2 to the $v = 1$ level increases the value of k by two orders of magnitude whereas the value of k is increased by less than a factor of 2 by excitation of HO to the $v = 2$ level,[3] despite the fact that excitation of the $H_2(v = 1)$ is only 52.7 kJ mol^{-1} whilst that of the $HO(v = 2)$ is 85.4 kJ mol^{-1}.

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

$\Delta H^\circ = -213.5$ 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			
$6.5 \times 10^{-31}(T/300)^{-2.9}[Ar]$	300–1500	CODATA, 1980[1]	(a)
$6.5 \times 10^{-31}[N_2]$	298		
$6.9 \times 10^{-31}(T/300)^{-1}[air]$	200–300	NASA, 1982[2]	(b)
$6.9 \times 10^{-31}(T/300)^{-0.8}[air]$	200–300	NASA, 1983[3]	(b)

Comments

(a) Based on unpublished data by Zellner.

(b) See comment (a).

(c) Value consistent with theoretical prediction by Patrick and Golden.[4]

Preferred Value

$k_0 = 6.9 \times 10^{-31}(T/300)^{-0.8}[N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.

$\Delta n = ^{+2}_{-0.8}$.

Comments on Preferred Value

Our previously preferred value referred to a much wider temperature range. The preferred value is still based on unpublished data which are in reasonable agreement with theoretical predictions. An independent experimental verification is required.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
3×10^{-11}	200–300	CODATA, 1980[1]	(a)
$1\times10^{-11}(T/300)^{-1.0}$	200–300	NASA, 1983[2]	(a)
$1\times10^{-11}(T/300)^{-1.0}$	200–300	NASA, 1983[3]	(a)

Comments

(a) See comment (a) for k_0.

Preferred Value

$k_\infty = 3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ over range 200–300 K.

Comments on Preferred Value

This value is still based on unpublished data such that an independent verification is required. A value of $F_c \simeq 0.72$ at 298 K is adopted.[4] Representation in the form $F_c = \exp(-T/T^*)$ leads to $T^* = 913$ K.

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$HO + HO_2(+M) \rightarrow H_2O + O_2(+M)$

$\Delta H^\circ = -291.3$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.1 \pm 1.2)\times10^{-11}$(1 Torr He)	299	Sridharan, Qiu, and Kaufman, 1981[1,2]	(a)
$(6.7 \pm 2.3)\times10^{-11}$(1.5–10.6 Torr He)	296	Temps and Wagner, 1982[3]	(b)
$(1.1^{+0.28}_{-0.39})\times10^{-10}$($\sim$760 Torr N_2)	298	Braun, Hofzumahaus, and Stuhl, 1982[4]	(c)
Relative Rate Coefficients			
$(6.1 \pm 1.0)\times10^{-11}$(2 Torr Ar)	298	Thrush and Wilkinson, 1981[5]	(d)
$(1\text{–}2)\times10^{-10}$(750 Torr SF_6)	298	Kurylo, Klais, and Laufer, 1981[6]	(e)
$(9.9 \pm 2.5)\times10^{-11}$(760 Torr He, Ar, N_2)	298	Cox, Burrows, and Wallington, 1982[7]	(f)
1.2×10^{-10}(730 Torr Ar, He; 1–5 Torr H_2O)	298	DeMore, 1982[8]	(g)
Reviews and Evaluations			
$(7 + 4P_{atm})\times10^{-11}$	200–300	NASA, 1982[11]	(h)
8×10^{-11}	298	CODATA, 1982[16]	(h)
$(7 + 4P_{atm})\times10^{-11}$	200–300	NASA, 1983[17]	(i)

Comments

(a) Discharge-flow study. HO_2 generated from $F + H_2O_2$. [HO] monitored by resonance fluorescence in presence of excess HO_2. Value originally[1] given as $k = (6.4 \pm 1.2)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} but later corrected[2] to the tabulated value.

(b) Discharge-flow study. HO generated by $F + H_2O$. Several sources of HO_2 used: $F + H_2O_2$, $HO + H_2O_2$, $H + O_2 + M$. [HO] and [HO_2] monitored by laser magnetic resonance.

(c) Flash photolysis of flowing N_2($\sim$760 Torr) containing a trace of H_2O. [HO] monitored by absorption at 308.2 nm. [HO] decay, accelerated by presence of O_2. k value obtained by modeling system. k apparently independent of H_2O pressure.

(d) Discharge-flow study. HO_2 generated from $H + H_2O_2$ and HO from $H + NO_2$. [HO] and [HO_2] monitored by laser magnetic resonance in presence of excess of H_2O_2. Measurement of steady-state concentration of HO_2 gives $k/k(HO + H_2O_2) = 36 \pm 6$. k obtained using $k(HO + H_2O_2) = 1.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

(e) Photolysis at 184.9 and 147 nm of H_2O^{18}–O_2 mixtures in presence of varied amounts of SF_6. $O^{16}O^{18}$ production measured mass spectrometrically. Extensive modeling scheme used to interpret results. Findings suggest that a linear HO–HO_2 complex is not formed.

(f) Low-frequency square-wave modulated photolysis of O_3–H_2O–M mixtures where M = He, Ar, or N_2. Steady-state [HO_2] measured at 210 nm. Computer fit of data to reaction scheme used to obtain k. $k(N_2) > k(Ar) > k(He)$ found but differences within experimental errors. Value of k unaffected H_2O pressure in range 1–16 Torr.

(g) Photolysis of H_2O–Ar or He mixtures containing trace quantities of O_2. Steady-state [HO] measured by laser resonance fluorescence. Diluent pressures varied in range 75–730 Torr. Values of $k/k(HO_2 + HO_2)^{1/2}$ obtained. k calculated using $k(HO_2 + HO_2)$ values, corrected for pressure and [H_2O] dependence, using the results of Hamilton and Lii[9] and Sander *et al.*[10] which are in close agreement with the CODATA recommendations. Variation of [H_2O] in range 1-5 Torr has no effect on value of k.

(h) Based on Sridharan *et al.*,[1,2] Kurylo *et al.*,[6] Temps and Wagner,[3] Thrush and Wilkinson,[5] Cox *et al.*,[7] DeMore,[8] Lii *et al.*,[12] Hochanadel *et al.*,[13] Burrows *et al.*,[14] Keyser.[15]

(i) Based on references cited in (c) plus Braun *et al.*[4]

Preferred Values

$k = (6.6 + a[M]) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and over range 0–760 Torr, where $a = 1.8 \times 10^{-19}$ cm^3 molecule^{-1} for M = He, Ar, N_2.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K and over range 0–760 Torr.

Comments on Preferred Values

Since our last evaluation, there have been further indirect measurements of k [4–8] and two direct determinations.[1,3] The recent results confirm the previously observed differences between high- and low-pressure values of k. Discharge-flow studies from a number of laboratories[1–5,15] are in excellent agreement with a value of $k = (6.6 \pm 1.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at a few Torr pressure and the studies at pressures close to one atmosphere[3,6–8,12–14] give values of k of about 1.1×10^{-11} cm^3 molecule^{-1} s^{-1}. The only study covering a wide pressure range is that of DeMore.[8] The method is indirect and the pressure effects on k are not clearly outside the experimental uncertainties, but a distinct trend in k was observed, from a value of 7.9×10^{-11} cm^3 molecule^{-1} s^{-1} at 75 Torr Ar to 1.2×10^{-10} cm^3 molecule^{-1} s^{-1} at 730 Torr Ar. Thus it now seems that, as for the $HO_2 + HO_2$ reaction, k is pressure dependent but, in contrast to $k(HO_2 + HO_2)$, the studies of Braun *et al.*,[4] and DeMore,[8] and Cox *et al.*[7] suggest that $k(HO + HO_2)$ is independent of H_2O concentration. This finding requires confirmation and more studies are also required to characterize the effects on k of pressure and temperature change and of various collision partners.

In making our recommendation, we assume that the rate constant is linearly dependent on pressure between the reasonably well characterized high- and low-pressure values.

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$HO + H_2O_2 \rightarrow H_2O + HO_2$

$\Delta H^\circ = -134.0$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.7 \pm 0.6) \times 10^{-12} \exp[-(260 \pm 50)/T]$	273–410	Wine, Semmes, and Ravishankara, 1981[1]	(a)
$(1.59 \pm 0.08) \times 10^{-12}$	297		
$(1.67 \pm 0.33) \times 10^{-12}$	296	Temps and Wagner, 1982[2]	(b)
$(2.93 \pm 0.49) \times 10^{-12} \exp[-(158 \pm 52)/T]$	250–370	Kurylo *et al.*, 1982[4]	(c)
$(1.79 \pm 0.14) \times 10^{-12}$	296		
$(1.81 \pm 0.24) \times 10^{-12}$	298	Marinelli and Johnston, 1982[6]	(d)
Reviews and Evaluations			
$3.1 \times 10^{-12} \exp(-187/T)$	200–300	NASA, 1982[5]	(e)
$2.9 \times 10^{-12} \exp(-160/T)$	240–460	CODATA, 1982[9]	(f)
$3.1 \times 10^{-12} \exp(-187/T)$	200–300	NASA, 1983[10]	(g)

Comments

(a) Laser flash photolysis (266 nm) of flowing H_2O_2–He or SF_6 mixtures. $[H_2O_2]$ monitored by photometry at 228.8 nm using absorption cross section of Molina and Molina.[3] [HO] monitored by resonance fluorescence.

(b) Fast flow-discharge study. HO generated by $F + H_2O$. [HO] monitored by laser magnetic resonance.

(c) Flash photolysis of flowing H_2O_2–H_2O–Ar mixtures. $[H_2O_2]$ monitored by photometry at 213.9 nm using absorption cross section recommended by the NASA Panel.[5] [HO] monitored by resonance fluorescence. Combining their results with the other available data,[1,7,8] recalculating the data where necessary using the absorption coefficient data recommended by the NASA Panel,[5] they obtain $k = (2.91 \pm 0.30) \times 10^{-12} \exp[-(161 \pm 32)/T]$.

(d) Laser flash photolysis of H_2O_2–Ar mixtures at 248.4 nm. [HO] monitored by time-resolved resonance fluorescence.

(e) Based on Wine *et al.*,[1] Kurylo *et al.*,[4] Sridharan *et al.*,[7] and Keyser.[8]

(f) Based on Sridharan *et al.*[7] and Keyser.[8]

(g) Based on references cited in (e) plus Marinelli and Johnston.[5]

Preferred Values

$k = 1.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.9 \times 10^{-12} \exp(-160/T)$ cm^3 molecule^{-1} s^{-1} over range 240–460 K.

Reliability

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

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

Comments on Preferred Values

The recent studies[1,2,4] are in excellent agreement with our previous recommendations which are unchanged and are identical with the values derived by Kurylo[4] from a least-squares fit to the available data.

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$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (1)
$HO_2 + HO_2(+M) \rightarrow H_2O_2 + O_2(+M)$ (2)

$\Delta H^\circ(1) = \Delta H^\circ(2) = -157.2$ 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			
$(2.97 \pm 0.45) \times 10^{-12}$(700 Torr N_2)	298	Sander *et al.*, 1982[1]	(a)
$k_1 = (1.6 \pm 0.2) \times 10^{-12}$			
$(2.5 \pm 0.1) \times 10^{-12}$(760 Torr N_2)	296	Simonaitis and Heicklen, 1982[3]	(b)
$k_1 = (1.4 \pm 0.2) \times 10^{-12}$			
$(1.5\text{–}2.0) \times 10^{-12}$(7–20 Torr O_2)	307	Thrush and Tyndall, 1982[6]	(c)
$2.4 \times 10^{-13} \exp[(560 \pm 200)/T]$(7-20 Torr O_2)	298–359	Thrush and Tyndall, 1982[7]	(d)
$(1.6 \pm 0.1) \times 10^{-12}$	298		
$(4.14 \pm 1.15) \times 10^{-13} \exp[(630 \pm 115)/T]$ (700 Torr N_2)	298–510	Patrick and Pilling, 1982[8]	(e)
$(3.66 \pm 0.46) \times 10^{-12}$	298		
$k_1 = 2.2 \times 10^{-13} \exp(620/T)$	230–420	Kircher and Sander, 1984[9]	(f)
$k_1 = (1.74 \pm 0.22) \times 120^{-12}$	298		
$k_2 = 1.9 \times 10^{-33}[M]\exp(980/T)$ ($M = N_2$, no H_2O)	230–420		
$k_2 = (5.4 \pm 3.1)[M] \times 10^{-32}$	298		
For effect of $[H_2O]$ see comment (f)			
$k_1 = (1.5 \pm 0.3) \times 10^{-12}$	295	Takacs and Howard, 1984[10]	(g)
Relative Rate Coefficients			
See comment (h)	298–373	Lii, Sauer, and Gordon, 1981[11]	(h)
Reviews and Evaluations			
$(3.4 + 2.5\,P/\text{atm}) \times 10^{-14} \exp(1150/T)$	200–300	NASA, 1982[12]	(i)
$4.5 \times 10^{-14} \exp(1200/T)$(1 atm, no H_2O)	275–400	CODATA, 1982[14]	(j)
$k_1 = 2.5 \times 10^{-13} \exp(560/T)$	200–300	NASA, 1983[15]	(k)
$k_2 = 1.7 \times 10^{-33}[M] \exp(1000/T)$			

Comments

(a) Flash photolysis of Cl_2–H_2–O_2 and Cl_2–CH_3OH–O_2 mixtures. $[HO_2]$ monitored by absorption at 227.5 nm. Value of σ_{HO_2} (227.5 nm) $= (3.0 \pm 0.40) \times 10^{-18}$ cm^3 $molecule^{-1}$ used was measured by same method as in earlier work.[2] Linear increase of k with increase of pressure found for all gases studied (He, Ar, N_2, O_2, SF_6) over range 0–700 Torr. Extrapolated value at zero pressure $= (1.6 \pm 0.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. Addition of H_2O enhances rate in approximately linear fashion independent of pressure of other gases. Behavior of DO_2 system is analogous. $k_H/k_D = 3.30 \pm 0.13$.

(b) Flash photolysis of Cl_2–CH_3OH–O_2 mixtures. $[HO_2]$ monitored by absorption at 220 nm. σ_{HO_2} taken from Cox and Burrows,[4] Paukert and Johnston.[5] k varies with pressure (He, N_2) over range 5–770 Torr. Extrapolated value of k at zero pressure $= (1.4 \pm 0.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

(c) Flash photolysis of Cl_2–CH_3OH–O_2 or Cl_2–H_2CO–O_2 mixtures. $[HO_2]$ monitored by infrared laser diode spectroscopy. Absolute concentration of HO_2 obtained from amount of Cl_2 depletion and assumption that each chlorine atom yields one HO_2. No pressure dependence of k observed over this small pressure range.

(d) Technique as in (c). Combining their results with those of Sander *et al.*[1] gives $k = (1.6 \times 10^{-12} + 6 \times 10^{-32}[M])$ cm^3 $molecule^{-1}$ s^{-1} for $M = N_2$, SF_6 at 298 K.

(e) Flash photolysis of Cl_2–CH_3OH–O_2 mixtures. $[HO_2]$ monitored by absorption at 227.5 nm.

(f) Technique as in (a). Rate coefficient measurements made at pressures between 100 and 700 Torr Ar and N_2. Enhancement of k by added water shown to contribute a multiplication term $(1 + 1.4 \times 10^{-21} \exp(2200/T)\,[H_2O])$ to the rate constant expression.

(g) Discharge-flow system at 1–7 Torr He. Laser magnetic resonance detection of HO_2, HO, and NO_2. HO_2 produced by $F + H_2O_2$, $Cl + H_2O_2$, and $CH_2OH + O_2$.

(h) Electron pulse radiolysis of H_2–O_2–H_2O mixtures. $[HO_2]$ monitored by absorption at 230 nm. Effect of $[H_2O]$ on k found to decrease with increase in temperature.

(i) Based on Sander *et al.*,[1] Simonaitis and Heicklen,[2] Cox and Burrows,[4] Lii *et al.*[11]

(j) Based largely on Cox and Burrows,[4] Lii *et al.*[13]

(k) Recommendation for k_1 based on Thrush and Tyndall,[6,7] Kircher and Sander,[9] Takacs and Howard.[10] Recommendation for k_2 based on Sander *et al.*,[1] Simonaitis and Heicklen,[3] Kircher and Sander.[9]

Preferred Values

$k_1 = 1.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2 = 5.4 \times 10^{-32}$ [N$_2$] cm^3 molecule^{-1} s^{-1} at 298 K.

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

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

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

Reliability

$\Delta \log k_1 = \Delta \log k_2 = 0.15$ at 298 K.

$\Delta (E_1/R) = +200$ K; $\Delta (E_2/R) = \pm 300$ K.

Comments on Preferred Values

Recent measurements, particularly those of Kircher and Sander, have clarified our understanding of this reaction. It appears that there are two channels available, a direct bimolecular channel (1), and a pressure-dependent channel (2).

For k_1 there is excellent agreement among the studies of Sander *et al.*,[1] Thrush and Tyndall,[7] Kircher and Sander,[9] and Takacs and Howard[10] both on its temperature dependence and its value at 298 K. k_2 is less well characterized. For our recommendation for k_2 we accept the results of Kircher and Sander[9] which are compatible with the work of Sander *et al.*[1] and Simonaitis and Heicklen.[3] For M = Ar, Kircher and Sander[9] obtain $k_1 = 2.3 \times 10^{-13} \exp(600/T)$ cm^3 molecule^{-1} s^{-1} and $k_2 = 8.4 \times 10^{-34} [\mathrm{Ar}] \exp(1100/T)$ cm^3 molecule^{-1} s^{-1}.

Water vapor has been shown to increase the rate.[9,11] The quantitative expression suggested by Kircher and Sander[9] for this effect, which we accept as our preferred value, requires confirmation.

In the work of Sahetchian *et al.*,[16] evidence was found for the formation of small amounts of H_2 in this system. This finding merits further study.

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4.3. Nitrogen Compounds

$$\begin{aligned} \mathrm{N} + \mathrm{NO_2} &\rightarrow \mathrm{N_2O} + \mathrm{O} && (1) \\ &\rightarrow \mathrm{NO} + \mathrm{NO} && (2) \\ &\rightarrow \mathrm{N_2} + \mathrm{O_2} && (3) \\ &\rightarrow \mathrm{N_2} + 2\mathrm{O} && (4) \end{aligned}$$

$\Delta H^\circ(1) = -175$ kJ mol^{-1}

$\Delta H^\circ(2) = -325$ kJ mol^{-1}

$\Delta H^\circ(3) = -506$ kJ mol^{-1}

$\Delta H^\circ(4) = -8$ kJ mol^{-1}

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

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.01 \pm 0.33) \times 10^{-12}$	293	Clyne and Ono, 1982[1]	(a)
Reviews and Evaluations			
1.4×10^{-12}	298	CODATA, 1982[2]	(b)
1.4×10^{-12}	298	NASA, 1982[3]	(b)
3.0×10^{-12}	298	NASA, 1983[4]	(c)

Comments

(a) Discharge flow–resonance fluorescence detection of N atoms. Pseudo-first-order conditions with $[NO_2]/[N] > 80$.

(b) Based on room-temperature result of Clyne and McDermid, 1975.[5]

(c) Based on room-temperature result of Clyne and Ono, 1982.[1]

Preferred Values

$k = 3.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 1$.

Reliability

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

Comments on Preferred Values

The preferred values of k at 298 K is based upon the recent result of Clyne and Ono.[1] This is a factor of 2 higher than previous results from the same laboratory.[5] However, the authors consider the recent result to be more reliable. Husain and Slater[6] reported a rate constant which is a factor of 12 higher. This high value may indicate the presence of catalytic cycles as discussed by Clyne and McDermid[5] and Clyne and Ono.[1] There have been no studies of the temperature dependence of k. The reaction products are taken to be $N_2O + O$ based on the results of Clyne and McDermid.[5] However, the reaction mechanism needs to be confirmed, as does the value of the rate constant.

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

$\Delta H^\circ = -306.2$ 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			
$8.8 \times 10^{-32}(T/300)^{-1.44}[N_2]$	200–370	Schieferstein, Kohse-Höinghaus, and Stuhl, 1983[1]	(a)
Reviews and Evaluations			
$1.2 \times 10^{-31}(T/300)^{-1.8}[N_2]$	200–300	CODATA, 1982[2]	(b)
$1.2 \times 10^{-31}(T/300)^{-1.8}[\text{air}]$	200–300	NASA, 1982[3]	(b)
$1.2 \times 10^{-31}(T/300)^{-1.8}[\text{air}]$	200–300	NASA, 1983[4]	(c)

Comments

(a) Laser flash photolysis of NO at 160 nm for generation of O atoms, NO_2 formation detected by NO_2 chemiluminiscence. Relative efficiencies of M, N_2: He: NO: $CH_4 = 1.00: 0.70: 1.43: 1.31$. Evaluation of rate constants in terms of theory by Troe, 1979[5] gives collision efficiencies which are close to, but slightly smaller than unity, in contrast to earlier results. A theoretical analysis accounting for contribution of electronically excited states by Smith[6], estimates an about 70% increase in k_0 due to excited states, thus decreasing collision efficiencies to typical values.

(b) Average of data from Michael, Payne, and Whytock, 1976[7] and Atkinson, Perry, and Pitts, 1977.[8]

Preferred Values

$k_0 = 1.0 \times 10^{-31}(T/300)^{-1.6}[N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 300 K.

$\Delta n = \pm 0.3$.

Comments of Preferred Values

Average from data of Refs. 1 and 7. No new data on high-pressure rate coefficients and intermediate falloff range, for older data see CODATA, 1980.[9]

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$$\begin{aligned} \mathbf{NH_2 + NO} &\mathbf{\rightarrow N_2 + H_2O} && \mathbf{(1)} \\ &\mathbf{\rightarrow N_2H + HO} && \mathbf{(2)} \\ &\mathbf{\rightarrow N_2 + H + HO} && \mathbf{(3)} \\ &\mathbf{\rightarrow N_2OH + H} && \mathbf{(4)} \\ &\mathbf{\rightarrow NH_2NO} && \mathbf{(5)} \end{aligned}$$

$\Delta H^\circ(1) = -517$ kJ mol^{-1}
$\Delta H^\circ(2) = ?$
$\Delta H^\circ(3) = -18$ kJ mol^{-1}
$\Delta H^\circ(4) = ?$

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.77 \pm 0.89)\times 10^{-7}(T)^{1.67}$	216–480	Stief *et al.*, 1982[1]	(a)
$(2.10 \pm 0.31)\times 10^{-11}$	298		
$4.4\times 10^{-5}(T)^{-2.3}\exp(-684/T)$	294–1215	Silver and Kolb, 1982[2]	(b)
$(9.59 \pm 2.4)\times 10^{-12}$	298		
$(1.7 \pm 0.5)\times 10^{-11}$	295	Andresen *et al.*, 1982[3]	(c)
Branching Ratios			
$(k_2 + k_3)/k < 0.22$	298	Stief *et al.*, 1982[1]	(a)
$(k_2 + k_3)/k = 0.4 \pm 0.1$	298	Silver and Kolb, 1982[2]	(b)
$(k_3 + k_4)/k \leqslant 0.05$	298	Silver and Kolb, 1982[2]	
$k_1/k \geqslant 0.29$	298	Andresen *et al.*, 1982[3]	(c)
$k_2/k \geqslant 0.65$			
$(k_3 + k_4)/k \leqslant 0.05$			
Reviews and Evaluations			
$1.7\times 10^{-11}(T/298)^{-1.6}$	210–500	CODATA, 1982[4]	(d)
$1.6\times 10^{-11}(T/298)^{-1.5}$	210–500	NASA, 1982[5]	(e)

Comments

(a) Flash photolysis of NH_3. First-order decay of $[NH_2]$ in excess [NO] monitored by laser induced fluorescence at 570 nm. Value of k independent of pressure over range 2.5–10 Torr. Production of HO looked for by resonance fluorescence; found only under static conditions and attributed to outgassed H_2O. No HO detected under flow conditions, leading to upper limit for its production given in table.

(b) High-temperature fast flow reactor. NH_2 produced by reaction $F + NH_3$. First-order decay of $[NH_2]$ in excess [NO] monitored by laser induced fluorescence at 598 nm. Product HO detected by resonance fluorescence or by laser induced fluorescence. H atom production looked for by resonance fluorescence. Products also analyzed with mass spectrometer.

(c)Flow reactor. NH_2 radicals produced by laser photolysis of NH_3 at 193 nm. Rate constant determined from observed concentration—time profiles of vibrationally excited H_2O molecules. Temporal profiles of reaction products monitored by atomic resonance absorption, laser induced fluorescence and spectrally resolved infrared and visible fluorescence.

(d) Based on room-temperature data of Gordon *et al.*,[6] Gebring *et al.*,[7] Hancock *et al.*,[8] Sarkisov *et al.*,[9] and the temperature-dependent studies of Lesclaux *et al.*[10] and Hack *et al.*[11]

(e) Based upon studies referenced in comment (d) and the newer results of Stief *et al.*[1] and Silver and Kolb.[2] An Arrhenius expression [$k = 3.6\times 10^{-12}\exp(450/T)$cm^3 molecule^{-1} s^{-1}] was entered in the table of recommended values, but the T^n expression given above is a better representation of these data.

Preferred Values

$k = 1.6\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.6\times 10^{-11}(T/298)^{-1.5}$ cm^3 molecule^{-1} s^{-1} over range 210–500 K.

$k_1/k = 0.3$ at 298 K.

$k_2/k = 0.7$ at 298 K.

Reliability

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

$\Delta n = \pm 0.5$ over range 210–500 K.

$\Delta k_1/k = \Delta k_2/k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred value for k at 298 K is the mean of the values reported by Stief *et al.*,[1] Silver and Kolb,[2] Andresen *et al.*,[3] Gordon *et al.*,[6] Gehring *et al.*,[7] Hancock *et al.*,[8] Sarkisov *et al.*,[9] Lesclaux *et al.*,[10] and Hack *et al.*[11] The values reported in these studies range from $(8\text{–}27)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. They tend to separate into two groups: flash photolysis results and discharge flow results average 19×10^{-12} and 9×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively. This cannot be accounted for simply on the basis of a pressure effect as pressure ranges of the two types of studies overlapped and no individual study observed a pressure dependence. The preferred temperature dependence is derived from a weighted average of the data below 500 K in the four temperature-dependent studies (Stief *et al.*,[1] Silver and Kolb,[2] Lesclaux *et al.*,[10] and Hack *et al.*[11])

The preferred branching ratios are based predominantly on the results of Andresen *et al.*[3] These results are in substantial agreement with those of Silver and Kolb[2] in the importance of hydroxyl radical production and also the importance of channel 1. The high yields of HO reported in these studies are in conflict with the results of Stief *et al.*[1] This discrepancy needs to be resolved.

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$NH_2 + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.6 \pm 1.4)\times10^{-33}(T/295)^{-2.0}$[He]	295–353	Hack *et al.*, 1982[1]	(a)
Reviews and Evaluations			
$<3\times10^{-18}$	298	CODATA, 1982[2]	(b)
$<3\times10^{-18}$	298	NASA, 1983[3]	(b)

Comments

(a) Discharge flow-laser induced fluorescence detection of [NH_2] in excess [O_2]. Total pressure of 1.5–16 Torr He. Kinetic analysis indicated that NH_2 decay rate data are consistent with an association reaction between NH_2 and O_2 which is in its low-pressure third-order region.

(b) Upper limit based on results of Lesclaux and Demissy.[4]

Preferred Values

$k < 3\times10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is unchanged from the previous evaluation and is based on the upper limiting value reported by Lesclaux and Demissy.[4] It is suggested that the NH_2 decay observed by Hack *et al.*[1] is due to reaction with some other species present, probably HO_2. Lesclaux[5] restudied this reaction under low-pressure conditions similar to those of Hack *et al.*[1] and reported that there was no detectable reaction at room temperature.

References

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$NO + O_3 \rightarrow NO_2 + O_2$

$\Delta H^\circ = -200$ kJ mol^{-1}

Rate coefficient data

k /cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.6 \pm 0.8)\times 10^{-12} \exp[-(1435 \pm 64)/T]$	195–369	Michael, Allen, and Brobst, 1981[1]	(a)
$(2.0 \pm 0.2)\times 10^{-14}$	298		
$8.9\times 10^{-19}(T)^{2.2} \exp(-765/T)$	204–353	Borders and Birks, 1982[2]	(b)
$(1.72 \pm 0.04)\times 10^{-14}$	298		
Reviews and Evaluations			
$3.6\times 10^{-12} \exp(-1560/T)$	200–400	CODATA, 1982[3]	(c)
$2.2\times 10^{-12} \exp(-1430/T)$	200–300	NASA, 1982[4]	(d)
$1.8\times 10^{-12} \exp(-1370/T)$	200–300	NASA, 1983[5]	(e)

Comments

(a) Three independent low-pressure fast flow studies under pseudo-first-order conditions. Extent of reaction was monitored by NO_2 chemiluminescence under conditions of excess NO or excess O_3. In other experiments, the decay of [NO] in excess [O_3] was monitored by resonance fluorescence. The data from each study were in good agreement. The data showed significant curvature on an Arrhenius plot; value of E/R varied from 1258 K (195–260 K) to 1656 K (260–369 K).

(b) Dual flow tube technique with NO_2 chemiluminescence detection under pseudo-first-order conditions of [NO] decay in excess [O_3]. Authors claim this technique gives accurate value of E/R over temperature intervals as small as 10 K. Nonlinear Arrhenius behavior was observed with value of E/R increasing from a value of 1200 K at the lowest temperature to 1470 K at the highest temperatures.

(c) Based on least-squares analysis of the data from 200–400 K reported by Lippmann *et al.*,[6] Ray and Watson,[7] and Birks *et al.*[8]

(d) Based on least-squares analysis of the data from 195–304 K reported by Michael *et al.*,[1] Lippmann *et al.*,[6] Ray and Watson,[7] and Birks *et al.*[8]

(e) Based on least-squares analysis of the data from 195–304 K reported by Michael *et al.*,[1] Borders and Birks,[2] Lippmann *et al.*,[6] Ray and Watson,[7] and Birks *et al.*[8]

Preferred Values

$k = 1.8\times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$k = 1.8\times 10^{-12} \exp(-1370/T)$ cm^3 $molecule^{-1}$ s^{-1} over range 195–304 K.

Reliability

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

$\Delta (E/R) = \pm 200$ 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.*,[6] Ray and Watson,[7] and Birks *et al.*[8] with data at closely spaced temperatures reported in Borders and Birks[2] and in Lippmann *et al.*[6] being grouped to give equal weight to each of the five studies. The 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.*,[8] Clyne *et al.*,[9] and Clough and Thrush.[10] Michael *et al.*,[1] Birks *et al.*,[8] Clyne *et al.*,[9] and Schurath *et al.*[11] 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[12] and Bemand *et al.*[13] are in good agreement with the preferred value.

References

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HO + NO + M→HONO + M

$\Delta H^\circ = -208.8$ 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			
$(11 \pm 1)\times 10^{-31}[N_2]$	293	Burrows, Wallington, and Wayne, 1983[1]	(a)
Reviews and Evaluations			
$6.5\times 10^{-31}(T/300)^{-2.4}[N_2]$	200–440	CODATA, 1982[2]	(b)
$6.7\times 10^{-31}(T/300)^{-2.5}$[air]	200–300	NASA, 1982[3]	(b)
$7.0\times 10^{-31}(T/300)^{-2.6}$[air]	200–300	NASA, 1983[4]	(c)

Comments

(a) Discharge flow-resonance fluorescence study at 1–5 Torr. Relative efficiencies of M, N_2: Ar: He = 1.00: 0.67: 0.55.

(b) Average from five earlier studies excluding the highest k_0 value of 15×10^{-31} N_2 cm^3 molecule^{-1} s^{-1} from Harris and Wayne, 1975[5].

(c) Weighted average similar to (b).

Preferred Value

$k_0 = 7.4\times 10^{-31}(T/300)^{-2.6}[N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–440 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 300 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Value

The new measurement was averaged with the five earlier values used in CODATA, 1982.[2] The temperature coefficient recommended by NASA, 1983,[4] is accepted since it is based on a theoretical analysis[6] and is in agreement with experiment. No new data on high-pressure rate coefficients and intermediate falloff range are available, for older data see CODATA, 1980.[7] Calculations of F_c give $F_c = 0.77$ at 300 K.

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HO + NO$_2$ + M→HONO$_2$ + M

$\Delta H^\circ = -207$ 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			
$(2.7 \pm 0.2)\times 10^{-30}[N_2]$	295	Burrows, Wallington, and Wayne, 1983[1]	(a)
$(2.6 \pm 0.7)\times 10^{-30}[O_2]$			
$(1.58 \pm 0.04)\times 10^{-30}$[He]	246	Trevor, Black, and Barker, 1982[2]	(b)
Reviews and Evaluations			
$2.6\times 10^{-30}(T/300)^{-2.9}[N_2]$	200–300	CODATA, 1982[3]	(c)
$2.6\times 10^{-30}(T/300)^{-2.9}$[air]	200–300	NASA, 1982[4]	(c)
$2.6\times 10^{-30}(T/300)^{-3.2}$[air]	200–300	NASA, 1983[5]	(c),(d)

Comments

(a) Discharge flow–resonance fluorescence study at 1–5 Torr. Relative efficiencies of M, N_2: O_2: Ar: He: CO_2 = 1.00: 0.96: 0.59: 0.59: 1.67.

(b) Laser flash photolysis–resonance fluorescence technique, measurement at 15 Torr.

(c) Average of several measurements which are in excellent agreement.

(d) Temperature coeffficient taken from calculations of Patrick and Golden.[6]

Preferred Values

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

$k_0 = 2.2\times10^{-30}(T/300)^{-2.9}[O_2]$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 300 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The new measurements for $M = N_2$ are in excellent agreement with the older preferred values. The older data of Anastasi and Smith[7] for $M = O_2$ are confirmed. The preferred value is the average of data from Refs. 1 and 7. Calculations by Smith[8] suggest that 5% of the HNO_3 formation proceeds via excited triplet states.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\geqslant 3.0\times10^{-11}$	295	Robertshaw and Smith, 1982[9]	(a)
Reviews and Evaluations			
3.5×10^{-11}	200–300	CODATA, 1982[3]	(b)
$2.4\times10^{-11}(T/300)^{-1.3}$	200–300	NASA, 1982[4]	(c)
$2.4\times10^{-11}(T/300)^{-1.3}$	200–300	NASA, 1983[5]	(c)
5.2×10^{-11}	200–300	Cobos and Troe, 1984[10]	(d)

Comments

(a) Flash photolysis–laser induced fluorescence study with Ar pressures up to 4 atm and CF_4 pressures up to 8.6 atm.

(b) Extrapolation of falloff curves from pressures below 1 atm.

(c) Based on earlier RRKM model by Smith and Golden, 1978.

(d) Evaluation of falloff curves[9] in terms of theory by Troe, 1981,[12] leading to temperature-independent k_∞ over range 200–550 K and $k_\infty \propto T^{-0.4}$ over range 900–1100 K.

Preferred Value

$k_\infty = 5.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over range 200–400 K.

Comments on Preferred Value

The new measurements by Robertshaw and Smith[9] allow for a more reliable extrapolation[10] to k_∞ than was possible earlier.

Intermediate Falloff Range

From the preferred values one derives $[N_2] = 2.0\times10^{19}$ molecule cm^{-3}. The present preferred k_∞ value is consistent with a F_c value at 300 K of 0.43 calculated[10] by the use of simple bond fission falloff curves. Expressing F_c in the form $F_c = \exp(-T/T^*)$ leads to $T^* = 353$ K. Larger F_c values obtained by Patrick and Golden[5] [F_c(300 K) = 0.7] were based on rigid RRKM type calculations omitting rotational contributions.

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$HO + HONO_2 \rightarrow H_2O + NO_3$ (1)
$\rightarrow H_2O_2 + NO_2$ (2)

$\Delta H^\circ(1) = -75$ kJ mol^{-1}
$\Delta H^\circ(2) = -7$ 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			
$(1.25 \pm 0.13) \times 10^{-13}$	298	Ravishankara, Eisele, and Wine, 1982[1]	(a)
$(5.7 \pm 1.7) \times 10^{-15} \exp[(896 \pm 145)/T]$	228–298	Margitan and Watson, 1982[2]	(b)
$(1.19 \pm 0.12) \times 10^{-13}$	298		
$(1.05 \pm 0.40) \times 10^{-14} \exp[(759 \pm 100)/T]$	225–296	Kurylo, Cornett, and Murphy, 1982[3]	(c)
$(1.38 \pm 0.20) \times 10^{-13}$	296		
$(7.3 \pm 2) \times 10^{-15} \exp[(867 \pm 85)/T]$	251–403	Jourdain, Poulet, and LeBras, 1982[4]	(d)
$(1.25 \pm 0.07) \times 10^{-13}$	296		
$(1.52 \pm 0.43) \times 10^{-14} \exp[(644 \pm 79)/T]$	218–363	Marinelli and Johnston, 1982[5]	(e)
$(1.31 \pm 0.24) \times 10^{-1}$	298		
$(8.3 \pm 0.9) \times 10^{-15} \exp[(850 \pm 40)/T]$	240–370	Smith *et al.*, 1984[6]	(f)
$(1.36 \pm 0.04) \times 10^{-13}$	295		
$(2.0 \pm 0.4) \times 10^{-14} \exp[(430 \pm 60)/T]$	237–404	Connell and Howard, 1984[7]	(g)
$(8.4 \pm 1.2) \times 10^{-14}$	301		
Branching Ratio			
$k_1/k = 0.98 \pm 0.35$	298	Ravishankara, Eisele, and Wine, 1982[1]	(a)
1.17 ± 0.34	251		
$k_1/k = 1.03 \pm 0.05$	298	Jourdain, Poulet, and LeBras, 1982[4]	(d)
Reviews and Evaluations			
$1.5 \times 10^{-14} \exp(650/T)$	220–360	CODATA, 1982[8]	(h)
$9.4 \times 10^{-15} \exp(778/T)$	220–300	NASA, 1982[9]	(i)
$9.4 \times 10^{-15} \exp(778/T)$	220–300	NASA, 1983[10]	(i)

Comments

(a) Pulsed laser photolysis of HNO_3 at 248 nm. $[NO_3]$ monitored by absorption at 662 nm; $[HNO_3]/[OH] > 1000$. Value of k in table is for 50 Torr Ar; k was also measured at 60 Torr SF_6 and at 251 K. Data consistent with previous study in same laboratory.[11] Reaction stoichiometry determined by monitoring NO_3 produced and calculation of initial [HO] produced by photolysis of HNO_3.

(b) Flash photolysis. First-order decay of [HO] in excess $[HNO_3]$ monitored by resonance fluorescence. Authors did not report any Arrhenius expression, due to observed dependence of k upon both temperature and pressure. k was reported to increase by 10% from 20–100 Torr He at 298 K and by 40% over same pressure range at 238 K. The Arrhenius expression given in the table results from least-squares fit to the data reported for $T = 228$–298 K at 40 Torr He. Significant nonlinear Arrhenius behavior was observed above 298 K at each value of the total pressure. k was also determined at 20 Torr He and at 100 Torr He. For the linear portion of the Arrhenius plots (at and below 298 K) the following values of E/R are derived: -735 K (20 Torr He) and -1000 K (100 Torr He). Authors made linear extrapolations to zero pressure and reported E/R value of -700 K for data at and below 298 K.

(c) Flash photolysis. First-order decay of [HO] in excess $[HNO_3]$ monitored by resonance fluorescence. k was studied from 225–443 K and from 30–50 Torr Ar and SF_6. k was observed to exhibit significant nonlinear Arrhenius behavior above 296 K and no dependence on total pressure.

(d) Discharge flow–EPR detection of [HO] in excess $[HNO_3]$. Pressure ~1 Torr. k was reported to exhibit linear Arrhenius behavior over entire temperature range; however, a greater temperature dependence ($E/R = -1119$ K) is derived using only data at and below 298 K. The NO_3 produced was measured indirectly by adding excess NO and monitoring its removal by EPR. The ratio $[NO_3]_{\text{produced}}/[HO]_{\text{consumed}} = 1.03 \pm 0.05$.

(e) Flash photolysis–resonance fluorescence detection of [HO] in excess $[HNO_3]$. Pressure of 10–50 Torr Ar. k was reported to exhibit linear Arrhenius behavior over entire temperature range, however a greater temperature dependence ($E/R = -697$ K) is derived using only data at and below 298 K.

(f) Flash photolysis–resonance fluorescence detection of [HO] in excess $[HNO_3]$. Pressure varied from 50–760 Torr He with no observed effect on value of k. Linear Arrhenius behavior was observed.

(g) Discharge flow–laser magnetic resonance detection of [HO] in excess $[HNO_3]$.

(h) Based on results of Wine *et al.*[11]

(i) Based on a least-squares fit to data reported by Wine *et al.*,[11] Ravishankara *et al.*,[1] Margitan and Watson,[2] Kurylo *et al.*,[3] Jourdain *et al.*,[4] and Marinelli and Johnston[5] at and below 300 K.

Preferred Values

$k = 1.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.4 \times 10^{-15} \exp(778/T)$ cm^3 molecule^{-1} s^{-1} over range 220–300 K.

$k_1/k = 1.0$ over range 220–300 K.

Reliability

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

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

Comments on Preferred Values

The preferred Arrhenius expression is based on a least-squares fit to the data at and below room temperature reported by Wine *et al.*,[11] Margitan and Watson[2] data at 40 Torr He, Kurylo *et al.*,[3] Jourdain *et al.*,[4] Marinelli and Johnston,[5] Smith *et al.*,[6] and Ravishankara *et al.*,[1] but did not use the data of Smith and Zelner,[12] Margitan *et al.*,[13] Nelson *et al.*,[14] and Connell and Howard.[7] The preferred Arrhenius expression was derived using only data from 220–300 K, due to the deviation from linearity above 300 K noted in recent studies. This nonlinear Arrhenius behavior can be rationalized in terms of an addition channel (dominating at low temperatures) and an abstraction channel (dominating at high temperatures). The data of Margitan and Watson[2] appear to be in good agreement with data reported in the other recent flash photolysis studies[1,3,5,6,11] but differs from them by exhibiting a small pressure dependence especially at low temperature. Although the low-pressure discharge flow results of Jourdain *et al.*[4] are in excellent agreement with results from the higher pressure flash photolysis studies below 300 K, this agreement does not preclude a small pressure dependence as the magnitude of the effect at temperatures greater than 250 K is small over the range 1 Torr (typical discharge flow tube pressure) to 40 Torr (typical flash photolysis pressure). The study by Nelson *et al.*[14] is considered to be superseded by the more comprehensive study in the same laboratory.[5] However, the reason for the difference between the results of Connell and Howard[7] and the preferred value is unknown. The room-temperature value in that study is consistent with earlier studies.[12,13]

It has been shown by Ravishankara *et al.*,[1] by Jourdain *et al.*,[4] and by Nelson *et al.*[14] that within experimental error the yield of NO_3 per HO removed is unity at 298 K. A similar product distribution has been reported for 250 K.[1] There is no evidence for production of H_2O_2.

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

$\Delta H^\circ(1) = -194$ kJ mol^{-1}

$\Delta H^\circ(2) = -50$ 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			
$(5.9 \pm 0.4) \times 10^{-13} \exp[(650 \pm 30)/T]$	240–340	Smith *et al.*, 1984[1]	(a)
$(5.24 \pm 0.19) \times 10^{-12}$	295		
Relative Rate Coefficients			
$(4.1 \pm 1.0) \times 10^{-12}$	295	Barnes *et al.*, 1981[2]	(b)
Reviews and Evaluations			
4.0×10^{-12}	246–324	CODATA, 1982[3]	(c)
$1.3 \times 10^{-12} \exp(380/T)$	240–340	NASA, 1982[4]	(d)
$1.3 \times 10^{-12} \exp(300/T)$	240–340	NASA, 1983[5]	(d)

Comments

(a) Flash photolysis–resonance fluorescence detection of HO in presence of excess $[HO_2NO_2]$ at 760 Torr He. HO_2NO_2 and impurity gas concentrations measured using FTIR spectroscopy.

(b) Relative study at 1 Torr N_2 in a 420 L reaction vessel using FTIR spectroscopy. The following ratios were measured: $k/k(HO + C_3H_6) = 0.268 \pm 0.026$ and $k(HO + C_3H_6)/k(HO + n\text{-}C_4H_{10}) = 5.9 \pm 0.6$. $k(HO + n\text{-}C_4H_{10})^{6-9}$ taken to be 2.6×10^{-12} cm^3 molecule^{-1} s^{-1}.

(c) Based on Trevor *et al.*[10]

(d) Based on Trevor *et al.*,[10] Smith *et al.*,[1] and Barnes *et al.*[2]

Preferred Values

$k = 4.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3 \times 10^{-12} \exp(380/T)$ cm^3 molecule^{-1} s^{-1} over range 240–340 K.

Reliability

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

$\Delta(E/R) = {}^{+270\text{ K}}_{-580\text{ K}}$.

Comments on Preferred Values

The preferred Arrhenius expression is derived using an unweighted least-squares fit to the data of Trevor *et al.*,[10] Smith *et al.*,[1] and Barnes *et al.*[2] Trevor *et al.*[10] in a low-pressure (3–15 Torr) laser flash-photolysis resonance fluorescence study recommended a temperature invariant value over the temperature range 246–324 K but also reported an Arrhenius expression with an E/R value of (193 ± 194) K. In contrast, Smith *et al.*[1] report a negative temperature dependence with an E/R value of $-(650 \pm 30)$ K. This difference may be due to the reaction being complex with different temperature dependences at low pressure[10] and at high pressure.[1] The error limits on the recommended E/R value encompass the results of both studies. At 220 K, the values deduced from the two studies differ by a factor of 3. Additional studies as a function of temperature and indentification of reaction products are needed.

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

$\Delta H^\circ = -97.7$ 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			
$(2.3 \pm 0.6) \times 10^{-31}(T/300)^{-4.6 \pm 1.0}[N_2]$	229–362	Sander and Peterson, 1984[1]	(a)
$(2.1 \pm 0.6) \times 10^{-31}(T/300)^{-4.6 \pm 1.0}[O_2]$			
Reviews and Evaluations			
$2.1 \times 10^{-31}(T/300)^{-5}[N_2]$	200–300	CODATA, 1982[2]	(b)
$2.3 \times 10^{-31}(T/300)^{-4.6}$[air]	200–300	NASA, 1982[3]	(c)
$2.3 \times 10^{-31}(T/300)^{-4.6}$[air]	200–300	NASA, 1983[4]	(c)

Comments

(a) Flash photolysis–uv absorption study in the pressure range 50–700 Torr. Extrapolation of falloff curves by the use of the formalism by Troe, 1979.[5] Relative efficiencies of M, N_2: O_2: He = 1.00: 0.92: 0.48. Strong enhancement of reaction in presence of water vapor, suggested to be due to formation of HO_2–H_2O complexes.

(b) Based on data by Howard, 1977[6] and Graham, Winer, and Pitts, 1978.[7]

(c) Based on data by Sander and Peterson, 1984[1] and Howard, 1977.[6]

Preferred Values

$k_0 = 2.3 \times 10^{-31}(T/300)^{-4.6}[N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

$k_0 = 2.1 \times 10^{-31}(T/300)^{-4.6}[O_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

New results in excellent agreement with earlier studies. T and M dependences are well characterized. Pressure dependence in good agreement with the data on the reverse reaction $HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$ from Graham, Winer, and Pitts, 1978.[7] Combination of forward and reverse reaction data[7] yields an equilibrium constant of $5.79 \times 10^{-28} \exp(11280/T)$ cm^3 molecule^{-1} s^{-1} in reasonable agreement with earlier data.

High-pressure rate coefficient
Rate coefficient data

k_∞ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.2 + 1.0) \times 10^{-12}(T/300)^{0.2 \pm 1.0}$	229–362	Sander and Peterson, 1984[1]	(a)
Reviews and Evaluations			
5×10^{-12}	200–300	CODATA, 1982[2]	(a)
4.2×10^{-12}	200–300	NASA, 1982[3]	(a)
4.2×10^{-12}	200–300	NASA, 1983[4]	(a)

Comments

(a) See comments for k_0.

Preferred Value

$k_\infty = 4.2 \times 10^{-12}(T/300)^{0.2}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Value

See comments for k_0; consistent extrapolation to k_∞ from several studies in good agreement.

Intermediate Falloff Range

Fit of falloff data to expressions from Ref. 4 leads to $F_c = 0.56 + 0.1$ at 300 K in agreement with calculations by Patrick and Golden.[6] The derived k_∞ value is based on $F_c = 0.56$. Representation in the form $F_c \simeq \exp(-T/T^*)$ leads to $T^* = 517$ K.

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$O + CH_3 \rightarrow HCHO + H$

$\Delta H^\circ = -285.4$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.14 \pm 0.29) \times 10^{-10}$	295	Plumb and Ryan, 1982[1]	(a)
Reviews and Evaluations			
1.4×10^{-10}	200–300	NASA, 1982[2]	(b)
1.3×10^{-10}	200–300	CODATA, 1982[3]	(b)
1.1×10^{-10}	200–300	NASA, 1983[4]	(c)

Comments

(a) Discharge-flow system with mass spectrometric analysis of [O] and [CH_3]; CH_3 generated from reaction $F + CH_4 \rightarrow HF + CH_3$ and k determined from pseudo-first-order decay of [CH_3] under conditions such that [O]$\gg$[CH_3].

(b) Based on data of Slagle, Pruss, and Gutman,[5] Washida and Bayes,[6] and Washida.[7]

(c) Weighted average of data of Washida and Bayes,[6] Washida,[7] and Plumb and Ryan.[1]

Preferred Value

$k = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

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

Comments on Preferred Value

Our previous recommendation[3] was based on the results of Slagle, Pruss, and Gutman,[5] Washida and Bayes,[6] and Washida.[7] All of these studies involved generating CH_3 from the reaction $O + C_2H_4$. It has recently been shown, however, that C_2H_3O is also a significant product of the $O + C_2H_4$ reaction.[8–11] It is not clear what effect this finding may have on the rate coefficient of the $O + CH_3$ reaction and consequently we have selected for the preferred value recent data of Plumb and Ryan,[1] which involves a more direct generation of CH_3 radicals.

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$O + CN \rightarrow CO + N(^2D)$ (1)
$\rightarrow CO + N(^4S)$ (2)

$\Delta H^\circ(1) = -92$ kJ mol^{-1}

$\Delta H^\circ(2) = -322$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.0×10^{-11}	298	Schacke, Schmatjko, and Wolfrum, 1973[1]	(a)
$(2.0 \pm 0.7) \times 10^{-11}$	275–387	Albers *et al.*, 1975[2]	(b)
$(1.8 \pm 0.5) \times 10^{-11}$	298	Schmatjko and Wolfrum, 1977[3]	(c)
$(1.7 \pm 0.7) \times 10^{-11}$	298	Schmatjko and Wolfrum, 1978[4]	(c)
Branching Ratios			
$k_1/k = 0.85 \pm 0.05$	298	Schmatjko and Wolfrum, 1977[3]	(c)
$k_1/k = 0.8 \pm 0.1$	298	Schmatjko and Wolfrum, 1978[4]	(c)
Reviews and Evaluations			
1.7×10^{-11}	298	Baulch *et al.*, 1981[5]	(d)

Comments

(a) Discharge-flash photolysis flow system. Decay of [CN] monitored by kinetic absorption spectroscopy at 421 nm. No change in rate constant for CN vibrationally excited up to $v = 6$.

(b) Flash photolysis flow reactor. First-order decay of [CN] monitored by kinetic absorption spectroscopy at 388 nm.

(c) Flash photolysis discharge flow system. [CO(v)] monitored by infrared absorption and [N] by vacuum ultraviolet absorption.

(d) Recommended value is based on results of Albers *et al.*[1] and other papers from same laboratory.

Preferred Values

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

$k_1/k = 0.8$ at 298 K.

Reliability

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

$\Delta (k_1/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

Preferred value accepts the value recommended in the recent review of Baulch *et al.*[5] It is based on results near room temperature by combined discharge flow–flash photolysis techniques reported by Albers *et al.*[2] and earlier results from the same laboratory.[1] For details, see Baulch's review.[5] The branching ratio data of Schmatjko and Wolfrum[4] is accepted; it indicates that reaction channel (1) is by far the more important pathway.

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4.4. Organic Compounds

$$\begin{array}{lr} O(^1D) + CH_4 \rightarrow HO + CH_3 & (1) \\ \rightarrow O(^3P) + CH_4 & (2) \\ \rightarrow H_2O + CH_2 & (3) \\ \rightarrow HCHO + H_2 & (4) \\ \rightarrow CH_3OH & (5) \end{array}$$

$\Delta H^\circ(1) = -179$ kJ mol^{-1}

$\Delta H^\circ(2) = -189$ kJ mol^{-1}

$\Delta H^\circ(3) = -220$ kJ mol^{-1}

$\Delta H^\circ(4) = -472$ kJ mol^{-1}

$\Delta H^\circ(5) = -564$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Branching Ratios			
$k_2/k = <0.040$	298	Wine and Ravishankara, 1982[1]	(a)
Reviews and Evaluations			
$k_1 = 1.4 \times 10^{-10}$	200–300	NASA, 1982[2]	(b)
$k_4 = 1.4 \times 10^{-11}$	200–300		
$k = 1.5 \times 10^{-10}$	200–300	CODATA, 1982[3]	(b)
$k_1/k = 0.9$	200–300		
$k_4/k = 0.1$	200–300		
$k_2/k = 0$	200–300		
$k_1 = 1.4 \times 10^{-10}$	200–300	NASA, 1983[4]	(b)
$k_4 = 1.4 \times 10^{-11}$	200–300		

Comments

(a) 248 nm laser flash photolysis of O_3–CH_4–He mixtures. Time-resolved measurement of $O(^3P)$ by resonance fluorescence detection.

(b) Based on data of Davidson *et al.*[5] and Amimoto *et al.*[6]

Preferred Values

$k = 1.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

$k_1/k = 0.9$; $k_4/k = 0.1$; $k_2/k = 0$ over range 200–300 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K; $\Delta k_1/k = \Delta k_4/k = \pm 0.1$.

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

Comments on Preferred Values

The new data[1] on this reaction are in excellent agreement with the previous recommendation[3] which is unaltered. Casavecchia *et al.*[7] 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.

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$HO + CH_4 \rightarrow H_2O + CH_3$

$\Delta H^\circ = -60.4$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.59 \pm 1.50) \times 10^{-12} \exp[(-1970 \pm 100)/T]$	278–473	Jeong and Kaufman, 1982[1]	(a)
$(7.9 \pm 0.5) \times 10^{-15}$	297		
$(7.66 \pm 0.64) \times 10^{-15}$	298	Husain, Plane, and Slater, 1982[2]	(b)
Relative Rate Coefficients			
$(1.38 \pm 0.7) \times 10^{-11} \exp[(-2440 \pm 225)/T]$	413–693	Baulch *et al.*, 1983[3]	(c)
3.8×10^{-15}	298*		
Reviews and Evaluations			
$3.2 \times 10^{-19} T^{2.4} \exp(-1060/T)$	200–2000	Cohen and Westberg, 1983[4]	
$2.4 \times 10^{-12} \exp(-1710/T)$	200–300	NASA, 1982[5]	(d)
$2.4 \times 10^{-12} \exp(-1710/T)$	200–300	CODATA, 1982[6]	(d)
$2.4 \times 10^{-12} \exp(-1710/T)$	200–300	NASA, 1983[7]	(d)

Comments

(a) Discharge-flow system; HO generated from $H + NO_2$ and [HO] monitored by resonance fluorescence.

(b) Flash photolysis–resonance fluorescence study; HO from H_2O.

(c) HO from steady-state photolysis of H_2O at 184.9 nm; relative rate coefficients, $k/k(HO + CO)$, obtained from measurements of CO_2 yields as function of $[CH_4]/[CO]$; based[8] on $k(HO + CO)$/cm^3 molecule^{-1} s^{-1} $= 1.1 \times 10^{-13} \exp(9.07 \times 10^{-4})T$; temperature coefficients quoted above obtained from least-mean-squares analysis of authors' rate coefficients.

(d) Based on data of Davis, Fischer, and Schiff.[9]

Preferred Values

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

$k = 2.4 \times 10^{-12} \exp(-1710/T)$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

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

Comments on Preferred Values

Recent experimental data[1-3] and a detailed evaluation[4] of this reaction confirm that the Arrhenius plot for this reaction is markedly curved over a wide range of temperature. For the low-temperature region (200–300 K) our previous recommendation[6] based on the data of Davis *et al.*[9] still stands. This is consistent with the new data[1-3] and with the previous results of Greiner,[10] Margitan *et al.*,[11] Zellner and Steinert,[12] and of Tully and Ravishankara.[13]

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$HO + C_2H_2 + M \rightarrow C_2H_2OH + M$ (1)
$\rightarrow CH_2CO + H + M$ (2)

$\Delta H^\circ(1) = -126$ kJ mol^{-1}.
$\Delta H^\circ(2) = -109$ kJ mol^{-1}.

Low-pressure rate coefficient
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3 \pm 1)\times 10^{-30}(T/300)^{+1.0}$[Ar]	297, 429	Perry and Williamson, 1982[1]	(a)
$(6 \pm 3)\times 10^{-30}$[He]	298	Hack *et al.*, 1983[2]	(b)
Reviews and Evaluations			
$3.5\times 10^{-29}(T/300)^{-3.5}$[air]	220–300	NASA, 1983[3]	(c)

Comments

(a) Flash photolysis of H_2O–C_2H_2 mixtures with Ar diluent (20–400 Torr). Flow system used to avoid accumulation of products. Pressure dependence of k observed in agreement with earlier work by Perry, Atkinson, and Pitts[4] and Michael *et al.*[5] Evaluation of fallout curve with roughly estimated $F_c = 0.5$ leads to the k_0 expression given here. No information on the nature of products obtained.

(b) Discharge flow system with ESR detection of HO radicals, or mass spectrometric product identification. Pressures around 2 Torr were used. By determination of the stoichiometry Δ [HO]/Δ [C_2H_2] $\lesssim 4$ of the reaction under these conditions, the rate coefficient k of the primary reaction could be deduced. By the use of data from Ref. 1 and $F_c = 0.5$, a falloff analysis of the measure k leads to the given k_0 value. Identification of the primary products showed that the adduct $(15 \pm 5\%)$ and $CH_2CO + H$ are the only products of the reaction at pressures around 2 Torr and at room temperature. This is in agreement with earlier results by Kanofsky *et al.*, 1974[6] at lower pressures.

(c) Based on data from Refs. 1, 4, and 5, and a calculation in terms of unimolecular rate theory. Typical relative efficiencies of N_2 versus Ar were used. This calculation apparently neglects the increase of k_0 with temperature which probably has to be attributed to a small barrier for complex formation.

Preferred Values

$k_0 = 2\times 10^{-29}(T/300)^{-1.3}[N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.
$\Delta n = \pm 2$.

Comments on Preferred Value

The preferred absolute value is a compromise between the NASA evaluation and the measurement of Ref. 2, assuming typical relative efficiencies of N_2 versus He. The high-pressure parts of the falloff curves measured in Refs. 1, 4, and 5 can be well reasonably related to the preferred k_0 value and the low-pressure measurement of Ref. 2 if the curvature of the k versus pressure plot is slightly modified. The preferred temperature coefficient is derived from the sum of the preferred temperature coefficient of k_∞, accounting for a small barrier for complex formation, and the NASA[3] temperature coefficient of k_0, apparently calculated neglecting this barrier. The temperature coefficient from Ref. 1 is not taken into consideration since these measurements require a long extrapolation of the falloff curves towards low pressures.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.91 \pm 0.90)\times 10^{-13}$	297	Perry and Williamson, 1982[1]	(a)
Reviews and Evaluations			
$6.5\times 10^{-12}\exp(-650/T)$ 7.3×10^{-13}	200–410 298	CODATA, 1982[7]	(b)
$8.0\times 10^{-13}(T/300)^{+2.6}$	200–300	NASA, 1983[3]	(b)

Comments

(a) See comment (a) to k_0. Given value for 400 Torr of Ar in agreement with earlier value.[4] New value for 429 K at 400 Torr slightly lower than earlier value.[4] Falloff corrections at 429 K may be necessary.

(b) Based on data from Michael *et al.*[5]

Preferred Value

$k_\infty = 6.5 \times 10^{-12} \exp(-650/T)$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

$k_\infty = 7.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

$\Delta (E/R) = \pm 350$ K.

Comments on Preferred Value

The new data from room temperature are consistent with the previous preferred value. The temperature coefficient remains uncertain. There appear two possibilities[1] either highly non-Arrhenius behavior as for HO + CO or a nearly straight Arrhenius plot. It appears that, at 1 atm and room temperature, the adduct C_2H_2OH is the main reaction product (>95%), $CH_2CO + H$ being the decomposition products of this adduct at low pressures when collisional stabilization becomes too slow.

Intermediate Falloff Range

The preferred k_0 and k_∞ values are based on an estimated value of $F_c = 0.5$.

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$HO + C_2H_4 + M \rightarrow C_2H_4OH + M$ (1)

$$\begin{aligned} HO + C_2H_4 + M &\rightarrow C_2H_4OH + M && (1)\\ &\rightarrow H_2CO + CH_3 + M && (2)\\ &\rightarrow CH_3CHO + H + M && (3)\\ HO + C_2H_4 &\rightarrow H_2O + C_2H_3 && (4) \end{aligned}$$

$\Delta H^\circ(1) = -123.4$ kJ mol^{-1}

$\Delta H^\circ(2) = -54.1$ kJ mol^{-1}

$\Delta H^\circ(3) = -39.3$ kJ mol^{-1}

$\Delta H^\circ(4) = -47.9$ 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			
3.5×10^{-29}[He]	298	Farquharson and Smith, 1980[1]	(a)
3.5×10^{-29}[He]	298	Tully, 1983[2]	(b)
5.5×10^{-29}[Ar]	296	Zellner and Lorenz, 1984[3]	(c)
Relative Rate Coefficients			
$(9.5^{+3.2}_{-2.4}) \times 10^{-29}$[air] $(5.9^{+3.0}_{-1.0}) \times 10^{-29}$[Ar]	295	Klein *et al.*, 1984[4]	(d)
Branching Ratios			
$k_2/k_0 \simeq 0.56$ at $[M] \rightarrow 0$ $k_3/k_0 \simeq 0.44$ $k_4/k_0 < 0.03$ at 2 Torr	295	Bartels, Hoyermann, and Sievert, 1982[5]	(e)
Reviews and Evaluations			
$3.7 \times 10^{-28}(T/300)^{-3.1}$[air]	200–300	NASA, 1983[6]	(f)

Comments

(a) Discharge flow–resonance fluorescence study at 0.4–0.7 Torr. Lindemann–Hinshelwood analysis of results leads to $k_0 = (3.1 \pm 0.5) \times 10^{-29}$[He] cm^3 molecule^{-1} s^{-1}. Higher value given here based on reevaluation with $F_c = 0.7$.

(b) Laser flash photolysis of N_2O–H_2O mixtures for HO generation, laser induced resonance fluorescence detection of HO. Higher end of the falloff curve at 50–600 Torr measured. Combined with earlier data by Howard[7] and Ref. 1, a consistent falloff curve for M = He can be derived. Temperature range 291–591 K.

(c) Laser flash photolysis for generation of HO, resonance fluorescence for detection of HO; pressure range 3–100 Torr, temperature range 296–524 K. Falloff extrapolation using $F_c = 0.8$.

(d) HO_2NO_2–NO system used as source of HO radicals. Reaction of HO with C_2H_4 studied in 420 L glass reactor relative to HO + n-hexane, where the latter reaction was calibrated against absolute measurements of the reaction HO + n-butane [k (295 K) $= 2.53 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}]. Pressure range 1–760 Torr, falloff curve constructed with $F_c = 0.7$.

(e) Discharge flow study at 0.1–2 Torr. Quantitative product analysis by mass spectrometry using molecular beam sampling. Measurements at 2 Torr give k_1: k_2: k_3: $k_4 = 0.21$: 0.44: 0.35: 0.025. Assuming $k_1 \rightarrow 0$ for $[M] \rightarrow O$, the given ratios are estimated.

(f) Theoretical prediction of k_0.

Preferred Values

$k_0 = 9.5 \times 10^{-29} (T/300)^{-3.1}$ [N_2] cm^3 molecule^{-1} s^{-1} over range 200–300 K.

$k_2/k_0 \simeq 0.56$.

$k_3/k_0 \simeq 0.44$.

Reliability

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

$\Delta n = \pm 2$.

Comments on Preferred Values

The new measurements,[1–4] together with older data, give a consistent set of falloff curves as demonstrated in Refs. 3 and 4. The data of Klein *et al.*[4] show particularly little scatter permitting the best extrapolation to k_0. The temperature coefficient calculated in the NASA evaluation[6] is adopted here. Although rate coefficients at pressures above 10 Torr are relatively insensitive to k_0, the quality of the data now appears sufficiently good to allow for a reliable extrapolation toward k_0.

High-pressure rate coefficient
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.47 \pm 0.24) \times 10^{-12}$	291	Tully, 1983[2]	(a)
$(3.3 \pm 1.3) \times 10^{-2} \exp[(320 \pm 150)/T]$	296–524	Zellner and Lorenz, 1984[3]	(b)
9.7×10^{-12}	298		
Relative Rate Coefficients			
$(8.48 \pm 0.39) \times 10^{-12}$	299	Atkinson *et al.*, 1982[7]	(c)
$(8.5 \pm 0.6) \times 10^{-12}$	295	Klein *et al.*, 1984[4]	(d)
Reviews and Evaluations			
$2.2 \times 10^{-12} \exp(400/T)$	250–500	CODATA, 1982[8]	(e)
8.0×10^{-12}	298		
8.8×10^{-12}	200–300	NASA, 1983[6]	(f)

Comments

(a) See comment (b) for k_0. Negative temperature coefficient of k_∞ suggested. It does, however, appear more probable to attribute this effect to falloff effects.

(b) See comment (c) for k_0. Extrapolating to k_∞ at high temperatures less certain because of increasing extent of falloff in the pressure range studied.

(c) Smog chamber study at atmospheric pressure; HO generated from photolysis of CH_3ONO in presence of air containing NO; relative rate coefficients determined from rate of disappearance of hydrocarbon reactants measured by gas chromatography. k/k (HO + cyclo-C_6H_{12}) $= 1.12 \pm 0.05$ evaluated with k (HO + cyclo-C_6H_{12}) $= 7.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 299 K.

(d) See comment (d) for k_0.

(e) Value from several studies at 1 atm, minor falloff correction neglected.

(f) Based on the same data as CODATA, 1982,[8] accounting for falloff effects. Positive temperatures coefficient of k_∞ considered improbable because of high value of k_∞ at 298 K.

Preferred Values

$k_\infty = 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over range 200–300 K.

Comments on Preferred Value

There is good agreement between older and recent studies of the falloff curve. The preferred value is based on the recent data,[2–5] and the earlier evaluations.[6,8] The temperature coefficient of k_∞ remains uncertain because of extensive falloff at temperatures above 300 K. None of the studies provided a sufficiently broad pressure range to account satisfactorily for these effects. Therefore, we follow the NASA evaluation[6] in assuming temperature independence of k_∞.

Intermediate Falloff Range

The falloff curves for N_2 at 300 K are consistent with $F_c = 0.7$. Expressed by $F_c = \exp(-T/T^*)$ this leads to $T^* = 840$ K.

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$HO + C_2H_6 \rightarrow C_2H_5 + H_2O$

$\Delta H^\circ = -89.5$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.6 \pm 0.4)\times 10^{-13}$	298	Leu, 1979[1]	(a)
$(2.31 \pm 0.40)\times 10^{-13}$	295	Lee and Tang, 1982[2]	(a)
$1.43\times 10^{-14}\ T^{1.05} \exp(-911/T)$	297–800	Tully, Ravishankara, and Carr, 1983[3]	(b)
$(2.59 \pm 0.21)\times 10^{-13}$	297		
Relative Rate Coefficients			
$(4.7 \pm 1.3)\times 10^{-11} \exp[(-1700 \pm 170)/T]$	403–683	Baulch *et al.*, 1983[4]	(c)
1.6×10^{-13}	298*		
Reviews and Evaluations			
$3.7\times 10^{-17}\ T^{1.9} \exp(-570/T)$	300–2000	Cohen and Westberg, 1983[5]	(d)
$1.9\times 10^{-11} \exp(-1260/T)$	200–300	NASA, 1982[6]	(e)
$1.9\times 10^{-11} \exp(-1230/T)$	290–500	CODATA, 1982[7]	(f)
$1.9\times 10^{-11} \exp(-1260/T)$	200–300	NASA, 1983[8]	(g)

Comments

(a) Discharge-flow system; HO from $H + NO_2$; [HO] monitored by resonance fluorescence under pseudo-first-order conditions.

(b) Flash photolysis of $Ar-H_2O-C_2H_6$ mixtures; [HO] monitored by resonance fluorescence under pseudo-first-order conditions; static reaction vessel.

(c) HO from steady-state photolysis of H_2O at 184.9 nm; relative rate coefficients, k/k (HO + CO) obtained from measurements of CO_2 yields as function of $[C_2H_6]/[CO]$ and from Baulch and Drysdale[9] k(HO + CO)/cm^3 molecule^{-1} s^{-1} = $1.1\times 10^{-13} \exp[(9.0\times 10^{-4})T]$; temperature coefficient quoted above obtained from least-mean-squares analysis of authors' rate coefficients.

(d) Based on data of Greiner,[10] Overend, Paraskevopoulos, and Cvetanovic,[11] Howard and Evenson,[12] and Tully, Ravishankara, and Carr.[3]

(e) Based on data of Greiner.[10]

(f) Based on data of Greiner,[10] Overend, Paraskevopoulos, and Cvetanovic,[11] and Howard and Evenson.[12]

(g) k at 298 K is average of data of Greiner,[10] Overend, Paraskevopoulos, and Cvetanovic,[11] Howard and Evenson,[12] Lee and Tang,[2] and Tully, Ravishankara, and Carr[3]; temperature coeffcient from data of Greiner,[10] and Tully, Ravishankara, and Carr.[3]

Preferred Values

$k = 2.7\times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.9\times 10^{-11} \exp(-1260/T)$ cm^3 molecule^{-1} s^{-1} over range 295–500 K.

Reliability

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

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

Comments on Preferred Values

Recent experimental data[2–4] and a detailed evaluation of this reaction[5] have confirmed that the rate coefficients display non-Arrhenius behavior over a wide range of temperatures. We have revised our recommended rate coefficient at 298 K by taking the mean of the rate coefficients of Greiner,[10] Overend, Paraskevopoulos, and Cvetanovic,[11] Howard and Evenson,[12] Leu,[1] Lee and Tang,[2] and Tully, Ravishankara, and Carr.[3] For temperatures up to 500 K, the Arrhenius equation is adequate and the recommended temperature coefficient was derived[8] from the data of Greiner,[10] and of Tully, Ravishankara, and Carr.[3]

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$$
\begin{array}{lr}
HO + C_3H_6 + M \rightarrow C_3H_6OH + M & (1) \\
\qquad \rightarrow C_2H_5CHO + H + M & (2) \\
\qquad \rightarrow H_2CO + C_2H_5 + M & (3) \\
\qquad \rightarrow CH_3COCH_3 + H + M & (4) \\
\qquad \rightarrow CH_3CHO + CH_3 + M & (5) \\
HO + C_3H_6 \rightarrow C_3H_5 + H_2O & (6)
\end{array}
$$

$\Delta H^\circ(1) = -135$ kJ mol^{-1}
$\Delta H^\circ(2) = -28.5$ kJ mol^{-1}
$\Delta H^\circ(3) = -60.2$ kJ mol^{-1}
$\Delta H^\circ(4) = -58.4$ kJ mol^{-1}
$\Delta H^\circ(5) = -79.8$ kJ mol^{-1}
$\Delta H^\circ(6) = -136.1$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data ($k_0 = k_2 + k_3 + k_4 + k_5$)

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
8×10^{-28}[Ar]	298	Zellner and Lorenz, 1984[2]	(a)
Relative Rate Coefficients			
8×10^{-27}[Ar] 8×10^{-27}[air]	298	Klein *et al.*, 1984[3]	(b)
Branching Ratios			
$k_2/k_3 = 1:4(\pm 1.5)$ at 0.2—1.8 Torr $k_4/k_5 = 1:3.5(\pm 1.5)$ at 0.2—1.8 Torr $k_6/k_0 < 0.05$ at 1.8 Torr	298	Hoyermann and Sievert, 1979[1]	(c)

Comments

(a) Laser flash photolysis generation of HO, resonance fluorescence detection of HO; pressure range 1–130 Torr. Falloff behavior detected, evaluated with $F_c = 0.8$.

(b) HO_2NO_2–NO system used as source of HO radicals. Reaction studied in 420 L glass reactor relative to HO + n-hexane, with the latter reaction calibrated against absolute measurements of the reaction HO + n-butane ($k = 2.53\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 295 K). Pressure range 1–760 Torr; falloff effects could be detected. Evaluation with $F_c = 0.5$ gives the present k_0 value.

(c) Identification of reaction mechanism and product yields in a nozzle reactor in the absence of wall or secondary reactions. Products detected by mass spectrometry. Pressure range <0.2 to 1.8 Torr. At 1.8 Torr adduct formation (1) leading to C_3H_3OH could be demonstrated.

Preferred Value

$k_0 = 8\times10^{-27}(T/300)^{-3.5}[N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 1$ over range 200–300 K.
$\Delta n = \pm 1$.

Comments on Preferred Value

In the pressure range 1–760 Torr at 298 K the reaction is close to its high-pressure limit. The falloff extrapolation, therefore, is very uncertain. We prefer the data from Klein *et al.*[3] which show little scatter. The temperature coefficient is estimated by analogy with the calculations for HO + C_2H_4, taken into account the larger molecular complexity. While the uncertainty in k_0 is fairly large, this has little relevance to k values near 1 atm. Nevertheless, at higher temperatures falloff effects become increasingly important.

High-pressure rate coefficients
Rate coefficient data ($k_\infty = k_1$)

k_∞ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.7×10^{-11} at 1 Torr	298	Morris, Stedman, and Niki, 1971[4]	(a)
1.45×10^{-11} at 20 Torr	298	Stuhl, 1973[5]	(b)
5.0×10^{-12} at 3 Torr	298	Bradley *et al.*, 1973[6]	(c)
5.0×10^{-12} at 1 Torr	300	Pastrana and Carr, 1975[7]	(d)
$4.1\times10^{-12}\exp(540/T)$ at 100 Torr	297–425	Atkinson and Pitts, 1975[8]	(e)
2.5×10^{-11} at 100 Torr	298		
$(2.63\pm0.12)\times10^{-11}$ at 200 Torr	298	Ravishankara *et al.*, 1978[9]	(f)
$(2.47\pm0.25)\times10^{-11}$ at 1 atm	297	Nip and Paraskevopoulos, 1979[10,11]	(g)
$(1.9\pm0.3)\times10^{-11}$ at 3 Torr	298	Smith, 1983[12]	(h)
$(3.0\pm0.5)\times10^{-11}$	298	Zellner and Lorenz, 1984[2]	(i)
Relative Rate Coefficients			
$(2.9\pm0.6)\times10^{-11}$ at 1 atm	305	Lloyd *et al.*, 1976[13]	(j)
$(2.4\pm0.3)\times10^{-11}$ at 1 atm	300	Cox, Derwent, and Williams, 1980[14]	(k)
$(1.5\pm0.2)\times10^{-11}$ at 1 Torr	295	Barnes *et al.*, 1981[15]	(l)
$(2.92\pm0.1)\times10^{-11}$ at 1 atm	297	Ohta, 1983[16]	(m)
$(3.0\pm0.2)\times10^{-11}$	295	Klein *et al.*, 1984[3]	(n)

Comments

(a) Discharge flow system with mass spectrometric detection. Carrier gas He at pressure of 1 Torr. Near the high-pressure limit; results fit falloff curve in Ref. 3.

(b) HO radicals generated by vacuum uv photolysis of H_2O. Detection of HO by resonance fluorescence. Results in disagreement with falloff curve in Ref. 3.

(c) Discharge flow system with ESR detection at about 3 Torr. Rate coefficient divided by measured stoichiometry of 3. Results in disagreement with falloff curve in Ref. 3.

(d) Discharge flow reactor, carrier gas He at 1 Torr. HO generated by reaction $H + NO_2 \rightarrow HO + NO$, HO followed by resonance absorption. Stoichiometry n determined. Given value for $n\times k$. Results in disagreement with falloff curve in Ref. 3.

(e) Flash photolysis–resonance fluorescence study in Ar over pressure range 25–100 Torr. Negative temperature coefficient probably due to increasing falloff at higher temperatures.

(f) Flash photolysis–resonance fluorescence study in He at 20 and 200 Torr.

(g) Flash photolysis–resonance fluorescence technique. HO formed from flash photolysis of N_2O–H_2 mixtures in Ar.

(h) Discharge flow–resonance fluorescence technique; carrier gas He in the pressure range 0.9–3 Torr; temperature range studied 255–458 K. No pressure dependence of k observed from 0.9 to 3 Torr in contrast to a prediction based on $k_0 = 4\times10^{-27}[\mathrm{He}]$ cm^3 molecule^{-1} s^{-1} and $F_c = 0.6$. Hence it was concluded that the high-pressure limit is established at 3 Torr. While this conclusion is not confirmed in the falloff study of Ref. 3, the given rate coefficient fits well to the falloff curve for M = He from Ref. 3. The temperature dependence of $k = 2.3\times10^{-11}(T/300)^{-4.4}$ cm^3 molecule^{-1} s^{-1}, measured between 255–458 K at a pressure of 3 Torr was attributed to falloff effects at higher temperatures.

(i) As comment (a) of k_0. Measurements in the pressure range 1–100 Torr of the carrier gas Ar lead to an extrapolated high-pressure value as given in the table (extrapolation with $F_c = 0.8$). The measurements at 1 and 100 Torr as well as the derived value of k_∞ are in good agreement with the falloff curve from Ref. 3.

(j) Smog chamber experiments at 1 atm of air. Measurements relative to OH + n-butane, evaluated with k (OH + n-butane) = 3×10^{-12} cm^3 molecule^{-1} s^{-1}.

(k) HO generated from steady-state photolysis of HONO in air in presence of NO, NO_2, and organic substances. Analysis of organic species by gas chromatography. Measurements evaluated relative to HO + C_2H_4 for which $k(HO + C_2H_4) = 8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} was used.

(l) Thermal source of HO radicals provided by decomposition of peroxynitric acid and subsequent reaction $HO_2 + NO \rightarrow NO_2 + HO$. Studies in a 420 L glass reaction chamber in the presence of hydrocarbon species using FTIR spectroscopy for analysis. HO + C_3H_6 measured relative to HO + n-C_4H_{10}. For 1 Torr, $k(HO + C_3H_6)/k$ (HO + n-

$C_4H_{10}) = 5.9 \pm 0.6$ was determined. Evaluation with $k(HO + n\text{-}C_4H_{10}) = 2.6 \times 10^{-12}$ cm^3 molecule^{-1} leads to value given in the table.

(m) HO generated by steady-state photolysis of H_2O_2 in presence of a mixture of two reactants, 10 Torr of O_2, and 750 Torr of N_2. Analysis by gas chromatography. Rate coefficient measured relative to HO + 1,3-butadiene, evaluation based on k (OH + 1,3-butadiene) $= 6.85 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(n) As comment (b) of k_0. Measurements over pressure range 1–760 Torr in Ar or air gives a very smooth falloff curve allowing satisfactorily for extrapolation to k_∞. k(1 atm)$\simeq 0.95\ k_\infty$.

Preferred Value

$k_\infty = 3.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.1$ over range 200–300 K.

Comments on Preferred Value

There is now excellent agreement for k_∞ at 298 K. Earlier discrepancies were in part due to the neglect of falloff effects, in part owing to complex secondary mechanism at low pressures. Studies of the temperature dependence of k_∞ so far have been limited to narrow pressure ranges such that falloff effects could not satisfactorily be separated from possible temperature coefficients of k_∞. At present there is no evidence of major temperature coefficients of k_∞. Therefore, we assume a temperature-independent k_∞.

Intermediate Falloff Range

Although falloff effects in the range 1–760 Torr at 298 K are more sensitive to k_0 than to F_c, a theoretical calculation of F_c should be undertaken. The presently preferred k_0 and k_∞ values, together with an estimated F_c value of $F_c = 0.5$, lead to a satisfactory representation of the majority of recent results in the falloff range. A representation $F_c = \exp(-T/T^*)$ gives $T^* = 433$ K.

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$$HO + C_3H_8 \rightarrow H_2O + n\text{-}C_3H_7 \quad (1)$$
$$\rightarrow H_2O + i\text{-}C_3H_7 \quad (2)$$

$\Delta H^\circ(1) = -82.3$ kJ mol^{-1}
$\Delta H^\circ(2) = -100.7$ 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			
$(1.20 \pm 0.2)\times 10^{-11} \exp[(-680 \pm 40)/T]$	296–497	Greiner, 1967, 1970[1]	(a)
$(1.4 \pm 0.2)\times 10^{-12}$	298		
$(8.3 \pm 0.2)\times 10^{-13}$	298	Bradley *et al.*, 1973[2]	(b)
$(1.98 \pm 0.08)\times 10^{-12}$	329	Harker and Burton, 1975[3]	(c)
$(2.02 \pm 0.10)\times 10^{-12}$	295	Overend, Paraskevopoulos, and Cvetanovic, 1975[4]	(d)
$(2.2 \pm 0.1)\times 10^{-12}$	381	Gordon and Mulac, 1975[5]	(e)
$(1.9 \pm 0.1)\times 10^{-12}$	416		
$1.59\times 10^{-15}T^{1.40} \exp(-428/T)$	297–690	Tully, Ravishankara, and Carr, 1984[6]	(f)
$(1.05 \pm 0.04)\times 10^{-12}$	297		
Relative Rate Coefficients			
2.1×10^{-12}	298	Gorse and Volman, 1974[7]	(g)
1.9×10^{-11}	926	Hucknall, Booth, and Sampson, 1975[8]	(h)
$(1.50 \pm 0.22)\times 10^{-12}$	300	Darnall, Atkinson, and Pitts, 1978[9]	(i)
8.7×10^{-12}	753	Baldwin and Walker, 1979[10]	(j)
$(1.22 \pm 0.05)\times 10^{-12}$	299	Atkinson *et al.*, 1982[11]	(k)
$(4.1 \pm 1.2)\times 10^{-11} \exp[(-1340 \pm 140)/T]$	428–696	Baulch *et al.*, 1983[12]	(l)
4.5×10^{-13}	298*		
Reviews and Evaluations			
$1.6\times 10^{-11} \exp(-800/T)$	200–300	NASA, 1982[13]	(m)
$7.0\times 10^{-22} T^{3.4} \exp(590/T)$	300–2000	Cohen and Westberg, 1983[14]	(n)
$1.6\times 10^{-11} \exp(-800/T)$	200–300	NASA, 1983[15]	(m)

Comments

(a) Flash photolysis of H_2O–Ar–C_3H_8 mixtures at a pressure of 100 Torr; [HO] monitored by uv absorption spectroscopy using photographic detection.

(b) Discharge-flow system; HO generated from H + NO_2; [HO] monitored by ESR detection; stoichiometry obtained from mass spectrometric analysis.

(c) Molecular modulation spectroscopic study; HO generated from O + C_3H_8; [HO] monitored by uv absorption at 307–309 nm; reaction studied over pressure range 100–300 Torr.

(d) Flash photolysis of H_2O–H_2–C_3H_8 mixtures at 50 Torr pressure; [HO] monitored by uv absorption spectroscopy.

(e) Pulse radiolysis of H_2O (1 atm) in presence of small quantities of C_3H_8; [HO] monitored by uv absorption spectroscopy.

(f) Flash photolysis of Ar–H_2O–C_3H_8 mixtures; [HO] monitored by resonance fluorescence under pseudo-first-order conditions; flow system.

(g) Static system photolysis of H_2O in presence of O_2–CO–C_3H_8; end-product analysis for CO_2; $k/k(HO + CO) = 14.3$ and from CODATA evaluation[16] $k(HO + CO) = 1.5\times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

(h) Static system; boric acid-coated vessel; HO from decomposition of H_2O_2; relative rate coefficients determined from consumption of hydrocarbons; $k/k(HO + C_2H_6) = 2.2$ at 926 K; based[14] on $k(HO + C_2H_6) = 8.66\times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 926 K.

(i) Smog chamber study; HO generated from photolysis of NO_x–RH–air mixture; relative rate coefficients determined from rate of disappearance of hydrocarbons (gas chromatography); $k/k(HO + n\text{-}C_4H_{10}) = 0.58$; based[9] on $k(HO + n\text{-}C_4H_{10}) = 2.58\times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 300 K.

(j) Static system; small amounts of C_3H_8 added to slowly reacting mixtures of $H_2 + O_2$; reaction rates following by consumption of C_3H_8 (gas chromatography) and by pressure change; relative rate coefficient $k/(HO + C_3H_8)/k(HO + H_2) = 9.9$; based[14] on $k(HO + H_2) = 8.79\times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 753 K

(k) Smog chamber study; HO generated from photolysis of CH_3ONO–RH–NO–air mixture; relative rate coefficients determined from rate of disappearance of hydrocarbons (gas chromatography); $k/k(HO + n\text{-}C_4H_{10}) = 0.473 \pm 0.016$; based[9] on $k(HO + n\text{-}C_4H_{10}) = 2.58\times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 300 K

(l) HO from steady-state photolysis of H_2O at 184.9 nm; relative rate coefficients, $k/k(\mathrm{HO}+\mathrm{CO})$ obtained from measurements of CO_2 yields as function $[C_3H_8]/[CO]$; based[17] on $k(\mathrm{HO}+\mathrm{CO})/\mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1} = 1.1\times10^{-13}\exp[(9.07\times10^{-4})T]$; temperature coefficient quoted above obtained from least-mean-squares analysis of authors' rate coefficients.

(m) k_{298} is average of data of Greiner,[1] Bradley *et al.*,[2] Tully, Ravishankara, and Carr,[3] and Gorse and Volman[7]; temperature coefficient from data of Greiner,[1] and Tully, Ravishankara, and Carr.[3]

(n) Based on data of Greiner[1] and of Baldwin and Walker.[10]

Preferred Values

$k = 1.2\times10^{-12}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ at 298 K.

$k = 1.6\times10^{-11}\exp(-800/T)\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ over range 290–500 K.

Reliability

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

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

Comments on Preferred Values

The room-temperature rate constants for this reaction are not in particularly good agreement, ranging from 0.83×10^{-12} to $2.2\times10^{-12}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$. The recommended rate coefficient at 298 K is the simple average of the values determined by Greiner,[1] Bradley *et al.*,[2] Tully, Ravishankara, and Carr,[6] Darnall, Atkinson, and Pitts,[9] and Atkinson *et al.*[11] The temperature coefficient for temperatures up to 500 K was derived[13] from a linear least-squares analysis of the rate coefficients of Greiner,[1] and of Tully, Ravishankara, and Carr,[6] with adjustment of the A factor to allow for the recommended rate coefficient at 298 K. The Arrhenius plot is markedly curved over a wide range of temperature.[6,12,14] The recommended room-temperature rate coefficient is also in agreement with the value predicted from the equation $k = (N_{\mathrm{prim}}\times6.5\times10^{-14} + N_{\mathrm{sec}}\times5.8\times10^{-13} + N_{\mathrm{tert}}\times2.1\times10^{-12})\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ at 300 K, where N_{prim}, N_{sec}, and N_{tert} are the numbers of primary, secondary, and tertiary C–H bonds in the alkane which react with the HO radicals.[9,10]

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HO + HCN→products

Rate coefficient data

$k/\mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.6\times10^{-11}\,T^{-1}\exp(-1860/T)$	298–563	Phillips, 1979[1]	(a)
1.0×10^{-16}	298		
See comment	373	Phillips, 1978[2]	(b)
$1.2\times10^{-13}\exp(-400/T)$	296–433	Fritz *et al.*, 1983[3]	(c)
$(3\pm1)\times10^{-14}$	298		
Reviews and Evaluations			
$1.2\times10^{-13}\exp(-400/T)$	200–300	NASA, 1983[4]	(d)

Comments

(a) Discharge flow–resonance fluorescence technique. Total pressure of 10–15 Torr He or Ar with no observed dependence of k on total pressure. Data analysis required numerical integration of complex set of rate equations for [OH] and [O].

(b) Discharge flow–resonance fluorescence technique. Strong falloff in value of k observed for pressures below 15 Torr down to about 3 Torr He or Ar. Mechanism involving a stabilized addition complex proposed. These experiments followed those reported in Phillips 1979.[1]

(c) Flash photolysis–resonance absorption technique. Total pressure varied over range 10–350 Torr N_2. Significant pressure dependence observed. Expression given is for high-pressure limit. Over the stated temperature range, a weak temperature dependence is observed, but a much stronger temperature dependence is observed at higher temperatures.

Preferred Values

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

$k = 1.2\times10^{-13}\exp(-400/T)$ cm^3 molecule^{-1} s^{-1} over range 296–433 K (1 atm).

Reliability

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

$\Delta (E/R) = \pm 300$.

Comments on Preferred Values

The preferred value accepts with widened error limits the recent results of Fritz *et al.*[1] Significant dependence of the rate coefficient on pressure was observed in this study, and the values given refer to the high-pressure limit. The authors conclude that the predominant pathway at low temperatures consists of the formation of an HCNOH complex by an addition process which is exothermic by at least 60 kJ mol^{-1}. At higher temperatures ($T > 500$ K), a strong temperature dependence is observed which is suggestive of a change in mechanism. The earlier results of Phillips[1,2] at low pressures were not considered in the derivation of the preferred value.

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$HO + CH_3CN \rightarrow H_2O + CH_2CN$

$\Delta H^\circ = -110$ kJ mol^{-1}

Rate coefficient

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.86\times10^{-13}\exp[-(755\pm125)/T]$	297–424	Harris, Kleindienst, and Pitts, 1981[1]	(a)
$(4.94\pm0.6)\times10^{-14}$	297		
$6.28\times10^{-13}\exp(-1030/T)$	250–363	Kurylo and Knable, 1984[2]	(b)
$(1.94\pm0.37)\times10^{-14}$	298		
Reviews and Evaluations			
$4.5\times10^{-13}\exp(-750/T)$	200–300	NASA, 1983[3]	(c)

Comments

(a) Flash photolysis–resonance fluorescence technique. First-order decay of [HO] monitored. Total pressure of 50 Torr Ar.

(b) Flash photolysis–resonance fluorescence technique. First-order decay of [HO] monitored. Rate coefficient independent of pressure over range 20–50 Torr Ar or 50 Torr SF_6.

(c) Based on result of Harris *et al.*[1] and unpublished room-temperature result of Zellner.

Preferred Values

$k = 3.4\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.7\times10^{-13}\exp(-890/T)$ cm^3 molecule^{-1} s^{-1} over range 250–420 K.

Reliability

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

$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The results of Harris *et al.*[1] are approximately a factor of 2 greater than those of Kurylo and Knable[2] over the common temperature range, and a least-squares fit to the individual data points results in an unrealistically high temperature dependence. The preferred value of E/R is the mean of the two reported values[1,2] and the A factor is derived from a fit to the preferred value of k at 298 K, which is taken as the mean of the room-temperature values reported in these studies.

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$HO + CO \rightarrow H + CO_2$

$\Delta H^\circ = -104.0$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.6) \times 10^{-13}$	298	Dreier and Wolfrum, 1981[1]	(a)
$(1.46 \pm 0.12) \times 10^{-13}$	298	Husain, Plane, and Slater, 1982[2]	(b)
$\exp(-30.03 + 1.22 \times 10^{-3} T)$	250–1040	Ravishankara and Thompson, 1983[3]	(c)
$(1.4 \pm 0.12) \times 10^{-13}$	298		
$\dfrac{6.14 \times 10^{-13} + 5.65 \times 10^{-16}(P_{N_2}/\text{Torr})}{4.1 + 9.2 \times 10^{-4}(P_{N_2}/\text{Torr})}$	298	Paraskevopoulos and Irwin, 1984[4]	(d)
Relative Rate Coefficients			
$1.5 \times 10^{-13}[1 + 0.4(P/\text{atm})]$	298	DeMore, 1984[5]	(e)
2.49×10^{-13}	299	Niki *et al.*, 1984[6]	(f)
Reviews and Evaluations			
$1.35 \times 10^{-13}(1 + P/\text{atm})$	200–300	NASA, 1982[7]	(g)
$1.5 \times 10^{-13}(P < 100\ \text{Torr})$	200–300	CODATA, 1982[8]	(h)
$1.5 \times 10^{-13}(1 + 0.6P/\text{atm})$	298	NASA, 1983[9]	(i)

Comments

(a) Discharge flow system; HO from $H + NO_2$; rate coefficients determined from CO_2 yields with corrections for HO loss by other reactions; above k is for a total pressure of 3 Torr; $HO + CO(v) \rightarrow H + CO_2$ reaction also studied by generating $CO(v)$ from reaction $N_2(v = 1) + CO \rightarrow N_2 + CO(v)$.

(b) Flash photolysis–resonance fluorescence study using flow system; HO from photolysis of H_2O–He mixtures; total pressure ~ 1.2 Torr.

(c) Flash photolysis–resonance fluorescence using flow system; HO from pulsed photolysis of H_2O–Ar at 165 nm; measurements at 100 Torr of Ar with varying CO pressures.

(d) Flash photolysis–resonance absorption system; HO from photolysis of H_2O in presence of He, N_2, CF_4, and SF_6 in pressure range 20–700 Torr; relative third body efficiencies estimated to be H_2O:SF_6:CF_4:N_2:He $= 1.0:0.5:0.3:0.1:0.02$. Addition of small amounts of O_2 caused HO decay to become nonexponential and slower, explained by reactions of HO_2 formed in the presence of O_2.

(e) Photolysis of H_2O–Ar or He mixtures; steady-state [HO] measured by laser resonance fluorescence values of $k/k(HO_2 + HO_2)^{1/2}$ obtained. k calculated using $k(HO_2 + HO_2)$ values, corrected for pressure and $[H_2O]$ dependence, which are in close agreement with CODATA recommendations.

(f) FTIR study of HO generated from photo-oxidation of RONO in presence of 700 Torr air in a competitive system with $^{13}C\,^{16}O$ or $^{12}C\,^{18}O$ and C_2H_4; rates measured from decay of C_2H_4 and formation of CO_2; $k/k(HO + C_2H_4) = 35.95 \pm 0.95$ for $^{13}C^{16}O$ and $k/k(HO + C_2H_4) = 36.30 \pm 0.84$ for $^{12}C\,^{18}O$ and based on $k(HO + C_2H_4) = 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (CODATA evaluation).

(g) Based on data of Overend and Paraskevopoulos,[10] Perry, Atkinson, and Pitts,[11] Biermann, Zetzsch, and Stuhl,[12] Cox, Derwent, and Holt,[13] and Butler, Solomon, and Snelson.[14]

(h) As for comment (g) along with data of Sie, Simonaitis, and Heicklen[15] and Chan *et al.*[16]

(i) Rate coefficient at zero pressure as for note (g) along with data of Dreier and Wolfrum,[1] Husain, Plane, and Slater,[2] and Ravishankara and Thompson.[3]

Preferred Values

For pressures < 100 Torr, $k = 1.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, over range 200–300 K.

For pressures 100–760 Torr (air), $k = 1.5 \times 10^{-13}$ $[1 + 0.45\,(P/\text{atm})]$ at 298 K.

Reliability

$\Delta \log k = \pm 0.05$ for low-pressure value at 298 K.

$\Delta \log k = \pm 0.1$ for 760 Torr (air) value at 298 K.

Comments on Preferred Values

The recent measurements of Dreier and Wolfrum,[1] of Husain, Plane, and Slater,[2] and of Ravishankara and Thompson,[3] are in excellent agreement with our previous recommendation[8] for this reaction in the low-pressure region.

The effect of pressure on the overall rate of oxidation of CO to CO_2 by HO has been reinvestigated by Paraskevopoulos and Irwin[4] and our preferred data for the pressure range 100–760 Torr are based on their measurements, which are in good agreement with the results of DeMore.[5] In addition these studies[4,5,17] have confirmed that pressure effects on the rate coefficient are observed in the absence of O_2.

Dreier and Wolfrum[1] report data on the reaction between HO and vibrationally excited CO; thus for vibrational temperatures of 1400 and 1800 K the rate coefficients for the reaction $HO + CO(v) \rightarrow H + CO_2$ at a total pressure of 3 Torr were found to be 1.4×10^{-13} and 1.3×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, respectively. This indicates that vibrational enhancement can be ruled out as an explanation of the non-Arrhenius behavior of this reaction which has been confirmed from the recent study of Ravishankara and Thompson[3] over a wide range of temperature. As before, however, the temperature coefficient, for conditions relevant to atmospheric modeling, can be considered to be zero.[8]

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$HO_2 + HCHO \rightarrow$ products

Rate coefficient data

k /cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.0×10^{-14}	298	Su *et al.*, 1979[1]; Su, Calvert, and Shaw, 1979[2]	(a)
7.5×10^{-14}	298	Veyret, Rayez, and Lesclaux, 1982[3]	(b)
Reviews and Evaluations			
4.5×10^{-14}	298	NASA, 1983[4]	(c)

Comments

(a) Photo-oxidation of $HCHO–Cl_2$ mixtures in H_2, O_2, and N_2 or in synthetic air (total pressure ~700 Torr) studied by FTIR spectroscopy; transient species $HOCH_2O_2H$ identified and ascribed to the mechanism; $HO_2 + HCHO \rightarrow HO_2CH_2O \rightarrow HOCH_2O_2$, $HO_2 + HOCH_2O_2 \rightarrow O_2 + HOCH_2O_2H$; k derived from computer modeling of complex system; for the reverse reaction, $HO_2CH_2O \rightarrow HO_2 + HCHO$, $k = 1.5$ s^{-1} was estimated at 298 K.

(b) Flash photolysis of $HCHO–O_2–NO$ mixtures at total pressures of 62–230 Torr; kinetic analysis based solely on $+\,d[NO_2]/dt$; k derived from computer modeling of complex system.

(c) Average value of data of Su *et al.*,[1,2] and Veyret *et al.*[3] with large assigned error limits ($\Delta \log k = \pm 1.0$).

Preferred Value

$k = 4.5\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 1.0$.

Comments on Preferred Value

While the evidence for the occurrence of the HO_2 addition reaction to HCHO appears to be reliable, the rate coefficients derived from computer modeling studies of complex systems are inconsistent. We have adopted the recommendation of the NASA Panel for the preferred rate coefficient at room temperature, which is the average of the data of Su *et al.*,[1,2] and Veyret *et al.*[3]

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$CH_3 + O_2 \rightarrow HCHO + HO$

$\Delta H^\circ = -215$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leqslant 3 \times 10^{-16}$	295	Plumb and Ryan, 1982[1]	(a)
$\leqslant 1 \times 10^{-16}$	298	Selzer and Bayes, 1983[2]	(b)
Reviews and Evaluations			
$< 1 \times 10^{-16}$	298	NASA, 1982[3]	(c)
$< 5 \times 10^{-17}$	298	CODATA, 1982[4]	(d)
$< 3 \times 10^{-16}$	298	NASA, 1983[5]	(c)

Comments

(a) Discharge-flow system with mass spectrometric analysis of $[CH_3]$; CH_3 generated from reaction $F + CH_4 \rightarrow HF + CH_3$; upper limit k based on the absence of HCHO, within the limits of detectability, in the products of $CH_3 + O_2$ reaction.

(b) Laser flash photolysis; $[CH_3]$ monitored by photoionization mass spectrometry; total pressure varied between 0.5 and 6 Torr; virtual absence of reaction $CH_3 + O_2 \rightarrow HCHO + HO_2$ was inferred from the plot of k $(CH_3 + O_2 + M \rightarrow CH_3O_2 + M)$ as function of pressure, which passed through the origin.

(c) Based on data of Baldwin and Golden[7] and Klais *et al.*[8]

(d) Based on data of Baldwin and Golden[7] and Klais *et al.*[8]

(e) As for comment (d) together with data of Plumb and Ryan[2] and Selzer and Bayes.[3]

Preferred Value

$k < 5 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

The recent studies of Plumb and Ryan[1] and of Selzer and Bayes[2] confirm that this is a very slow reaction and they are in agreement with our previous recommendation which is unaltered.

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$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$

$\Delta H^\circ = -129.6$ 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			
$(3.4 \pm 1.1) \times 10^{-31}$[He]	295	Plumb and Ryan, 1982[1]	(a)
$4.5 \times 10^{-31}[N_2]$	296	Selzer and Bayes, 1983[2]	(b)
Reviews and Evaluations			
$2.6 \times 10^{-31}(T/300)^{-3}[N_2]$	260–340	CODATA, 1982[3]	(c)
$2.2 \times 10^{-31}(T/300)^{-2.2}$[air]	200–300	NASA, 1982[4]	(c)
$6.0 \times 10^{-31}(T/300)^{-3}$[air]	200–300	NASA, 1983[5]	(d)

Comments

(a) Flow reactor with mass spectrometric sampling. He bath gas concentrations of $(2.5–25) \times 10^{16}$ molecule cm^{-3}. Falloff curve constructed with $F_c = 0.51$ collision efficiencies $\beta_c = 0.3$, and $k_\infty = 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(b) Laser flash photolysis of nitromethane with photoionization mass spectrometer detection of CH_3. Pressures in the range 0.5–6 Torr. Lower end of falloff curve observed with no sign of two-body reaction $CH_3 + O_2 \rightarrow CH_2O + OH$. A falloff extrapolation should be applied. Relative efficiencies of M, N_2: Ar: He = 1.00: 0.91: 0.58.

(c) Based on earlier data by Basco, James, and James[6], Parkes,[7] and Washida and Bayes,[8] which were obtained at higher pressures and with Lindemann–Hinshelwood falloff extrapolations. This procedure underestimates the limiting rate coefficients.

(d) Based on data from Refs. 1 and 2.

Preferred Value

$k_0 = 6 \times 10^{-31}(T/300)^{-2}[N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Values

The higher preferred value of this evaluation is based on the recent low-pressure data.[1,2] A full falloff curve can now be constructed with the confirmed k_∞ value.

High-pressure rate coefficient
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.8 \pm 0.4) \times 10^{-12}$	298	Hippler, Ravishankara, and Troe, 1984[9]	(a)
Reviews and Evaluations			
2×10^{-12}	200–400	CODATA, 1982[3]	(b)
$2 \times 10^{-12}(T/300)^{-1.7}$	200–300	NASA, 1982[4]	
$2 \times 10^{-12}(T/300)^{-1.7}$	200–300	NASA, 1983[5]	(c)

Comments

(a) Laser flash photolysis study using azomethane as CH_3 source and following CH_3 by uv absorption. Bath gases N_2, Ar, and O_2 varied between 0.1 and 160 atm. Nearly pressure-independent k at pressures above 10 atm.

(b) Based on earlier data at pressures below 1 atm by Van den Bergh and Callear,[10] Basco, James, and James,[6] Parkes,[7] Hochanadel *et al.*,[11] and Laufer and Bass.[12]

(c) As (b), temperature coefficient estimated.

Preferred Value

$k_\infty = 1.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over range 200–300 K.

Comments on Preferred Value

The new data up to 160 atm are in good agreement with the earlier extrapolated value. In contrast to the NASA evaluation[5] we estimate negligible temperature coefficient of k_∞.

Intermediate Falloff Range

The estimated value of $F_c - 0.51$ from Plumb and Ryan[1] is consistent with the measured falloff curve. Expressed by $F_c = \exp(-T/T^*)$ this leads to $T^* = 446$ K. From the preferred k_0 and k_∞ values one derives $[N_2]_c = 3 \times 10^{18}$ molecule cm^{-3}.

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$CH_3 + O_3 \rightarrow$ products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.4 \pm 1.5) \times 10^{-12} \exp[-(216 \pm 80)/T]$	243–384	Ogryzlo, Paltenghi, and Bayes, 1981[1]	(a)
$(2.61 \pm 0.23) \times 10^{-12}$	298		
Relative Rate Coefficients			
2.6×10^{-12}	221	Simonaitis and Heicklen, 1975[2]	(b)
4.8×10^{-12}	298		
5.6×10^{-13}	298	Washida, Akimoto, and Okuda, 1980[3]	(c)
Reviews and Evaluations			
$5.4 \times 10^{-12} \exp(-220/T)$	200–300	NASA, 1983[4]	(d)

Comments

(a) Flash photolysis of CH_3NO_2 at 193 nm in flow system with the carrier gas at ~2 Torr; $[CH_3]$ monitored by photoionization mass spectrometry under pseudo-first-order conditions; no analysis of products.

(b) Steady-state photolysis of O_3 in presence of CH_4–O_2 mixtures at total pressures of ~760 Torr; kinetic analysis of quantum yield measurements for the disappearance of O_3 yielded $k/k\,[CH_3 + O_2(+M) \rightarrow CH_3O_2(+M)] = 1.07$ at 221 K and 2.17 at 298 K; $k\,[CH_3 + O_2(+M) \rightarrow CH_3O_2(+M)] = 2.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

(c) Fast-flow system; CH_3 generated from $O + C_2H_4$; observed effect of O_3 on steady-state $[CH_3]$ (photoionization mass spectrometry) yielded $k/k\,[CH_3 + O(^3P)] = 5.1 \times 10^{-3}$; $k\,[CH_3 + O(^3P)] = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

(d) Based on data of Ogryzlo, Paltenghi, and Bayes.[1]

Preferred Values

$k = 2.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.4 \times 10^{-12} \exp(-220/T)$ cm^3 molecule^{-1} s^{-1} over the 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 taken from the direct measurements of Ogryzlo, Paltenghi, and Bayes.[1] The relative rate coefficients of Simonaitis and Heicklen[2] and of Washida, Akimoto, and Okuda,[3] are discounted since they are derived from complex systems. In the case of the system of Washida *et al.*,[3] the generation of CH_3 radicals from the reaction $O + C_2H_4$ is now known to introduce complications.[5-8]

The products of this reaction have yet to be established; on the basis of thermochemistry, several channels seem possible, e.g., (i) $CH_3O + O_2$ and (ii) $HCHO + H + O_2$.

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$CN + O_2 \rightarrow NCO + O$ (1)
$\rightarrow CO + NO$ (2)

$\Delta H^\circ(1) = -26$ kJ mol^{-1}
$\Delta H^\circ(2) = -455$ 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			
7.6×10^{-12}	298	Basco, 1965[1]	(a)
1.0×10^{-11}	298	Schacke, Schmatjko, and Wolfrum, 1973[2]	(b)
$5.3\times10^{-11}\exp[-(500\pm170)/T]$	275–398	Albers *et al.*, 1975[3]	(c)
1.0×10^{-11}	298		
$(2.0\pm0.1)\times10^{-11}$	298	Li, Sayah, and Jackson 1984[4]	(d)
Branching Ratios			
$k_2/k = 0.06 \pm 0.02$	298	Schmatjko and Wolfrum, 1978[5]	(e)
Reviews and Evaluations			
$4.0\times10^{-11}\exp(-450/T)$	290–400	Baulch *et al.*, 1981[6]	(f)

Comments

(a) Flash photolysis. Decay of [CN] in excess O_2 monitored by kinetic absorption spectroscopy at 388 nm.

(b) Flash photolysis flow reactor. Decay of [CN] monitored by kinetic absorption spectroscopy at 421 nm. Rate constant shown to decrease monotonically with increasing vibrational excitation of CN.

(c) Flash photolysis flow reactor. First-order decay of [CN] monitored by kinetic absorption spectroscopy at 388 nm; [NCO] monitored at 398 nm.

(d) Pulsed laser photolysis of C_2N_2 at 193 nm. First-order decay of [CN] monitored by laser induced fluorescence from individual rovovibronic level. Slightly higher rate constant reported for CN in $v = 1$ level.

(e) Product CO vibrationally excited up to $n = 4$ measured by resonance absorption spectroscopy.

(f) Recommended value is based on results of Albers *et al.*[3] and other flash photolysis results at room temperature.

Preferred Values

$k = 1.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.0\times10^{-11}\exp(-450/T)$ cm^3 molecule^{-1} s^{-1} over range 290–400 K.

$k_1/k = 0.94$ at 298 K.

Reliability

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

$\Delta(E/R) = \pm 450$ K.

$\Delta(k_1/k) = \pm 0.02$.

Comments on Preferred Values

The preferred value averages the recent room-temperature value of Li *et al.*[4] with the value recommended in the review of Baulch *et al.*[6] The latter is based on flash photolysis results at room temperature from Basco[1] and Schacke *et al.*[2] and the temperature-dependent results of Albers *et al.*[3] The branching ratio data of Schmatjko and Wolfrum[5] is accepted; it indicates that reaction channel (1) is the predominant pathway.

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$HCO + O_2 \rightarrow CO + HO_2$

$\Delta H^\circ = -137.5$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.0 \pm 0.8) \times 10^{-12}$	298	Reilly *et al.*, 1978[1]	(a)
$(4 \pm 1) \times 10^{-12}$	298	Nadtochenko, Sarkisov, and Vedeenev, 1979[2]	(b)
$(4.2 \pm 0.7) \times 10^{-12}$	298	Gill, Johnson, and Atkinson, 1981[3]	(c)
$5.5 \times 10^{-11}\, T^{-(0.4 \pm 0.3)}$	298–503	Veyret and Lesclaux, 1981[4]	(d)
$(5.6 \pm 0.6) \times 10^{-12}$	298		
Reviews and Evaluations			
$3.5 \times 10^{-12} \exp(140/T)$	200–300	NASA, 1982[5]	(e)
5.1×10^{-12}	298	CODATA, 1982[6]	(f)
$3.5 \times 10^{-12} \exp(140/T)$	200–300	NASA, 1983[7]	(e)

Comments

(a) Laser flash photolysis of CH_3CHO; [HCO] monitored by time-resolved intracavity dye laser detection.

(b) Flash photolysis of CH_3CHO and HCHO; [HCO] monitored by time-resolved intracavity dye laser detection.

(c) Flash photolysis of CH_3CHO; [HCO] monitored by time-resolved intracavity dye laser detection.

(d) Flash photolysis; HCO generated from photolysis of HCHO and CH CHO; [HCO] monitored by laser absorption under pseudo-first-order conditions.

(e) Average data of Washida, Martinez, and Bayes,[8] Shibuya *et al.*,[9] Veyret and Lesclaux,[4] and Langford and Moore.[11]

(f) Average data of Washida, Martinez, and Bayes,[8] Shibuya *et al.*,[9] and Clark, Moore, and Reilly.[10]

Preferred Values

$k = 5.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.5 \times 10^{-12} \exp(140/T)$ cm^3 molecule^{-1} s^{-1} over range 300–500 K.

Reliability

$\Delta (\log k) = \pm 0.2$ at 298 K.

$\Delta (E/R) = \pm 150$ K.

Comments on Preferred Values

The recommended rate constant at 298 K is the average of the results of Washida, Martinez, and Bayes,[8] Shibuya *et al.*,[9] and Veyret and Lesclaux.[4] The recommended temperature dependence is essentially that measured by Veyret and Lesclaux.[4] These recommendations discount the measurements of the rate coefficient based on the intercavity dye laser technique (Reilly *et al.*,[1] Nadtochenko, Sarkisov, and Vedeenev,[2] and Gill, Johnson, and Atkinson[3]). As pointed out in the NASA evaluation,[5,7] the consistently lower values of k derived by this technique could arise in several ways: (a) the relationship between [HCO] and laser attenuation might not be linear; (b) there could have been depletion of O_2 in the static systems used[4]; (c) the experiments were primarily designed for photochemical rather than kinetic studies.

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$CH_3O + NO_2 \rightarrow HCHO + HNO_2$ (1)
$CH_3O + NO_2(+M) \rightarrow CH_3ONO_2(+M)$ (2)

$\Delta H^\circ(1) = -235.9$ kJ mol^{-1}
$\Delta H^\circ(2) = -167.5$ kJ mol^{-1}

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

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$k_2 = 1.1 \times 10^{-11}$	363	Phillips and Shaw, 1965[1]	(a)
$k_2 = 7.4 \times 10^{-12}$	403	Baker and Shaw, 1965[2]	(b)
$k_2 = 1.5 \times 10^{-11}$	298	Wiebe *et al.*, 1973[3]	(c)
$k_2 = (1.0 \pm 0.5) \times 10^{-11}$	392–420	Datt and Rattray, 1979[4]	(d)
Branching Ratios			
$k_1/k_2 = 0.1$	403	Baker and Shaw, 1965[2]	(b)
$k_1/k_2 = 0.46$	303	Chao and Jaffe, 1972[5]	(e)
$k_1/k = 0.1 \pm 0.01$	298	Wiebe *et al.*, 1973[3]	(c)
$k_2/k = 0.9 \pm 0.1$	298		
$k_1/k_2 = 0$–0.5	384–424	Batt and Rattray, 1974[4]	(d)
Reviews and Evaluations			
$k_2 = 3.3 \times 10^{-13}$	300	Demerjian, Kerr, and Calvert 1974[6]	(f)
$k_1/k_2 = 0.1$	300		

Comments

(a) Thermal reaction in static vessel between CH_3CHO and NO–NO_2 mixtures in presence of MeC_4 at a total pressure of 50–250 Torr; relative rate coefficients based on analysis of CH_3ONO and CH_3ONO_2 by gas chromatography; $k(CH_3O + NO \rightarrow CH_3ONO)/k_2 = 1.8$ at 363 K; $k(CH_3O + NO \rightarrow CH_3ONO) = 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K (CODATA evaluation).

(b) Static reaction vessel; CH_3O generated from thermal decomposition of CH_3OOCH_3 in presence of NO–NO_2 mixtures; at total pressure of 83–140 Torr; same approach as comment (a); $k(CH_3O + NO \rightarrow CH_3ONO)/k_2 = 2.7$ at 403 K; $k(CH_3O + NO \rightarrow CH_3ONO) = 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K (CODATA evaluation).

(c) Steady-state photolysis of CH_3ONO in presence of NO–O_2 and NO–NO_2–N_2 mixtures at 8–350 Torr; relative rate coefficients derived from ϕ CH_3ONO_2; $k(CH_3O + NO)/k_2 = 1.3$ at 298 K; $k(CH_3O + NO \rightarrow CH_3ONO) = 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K (CODATA evaluation).

(d) Static reaction vessel; CH_3O from pyrolysis of CH_3OOCH_3 in presence of NO–NO_2–CF_4 at total pressure of ~513 Torr; relative rate coefficients determined from end-product analysis of CH_3ONO and CH_3ONO_2 (gas chromatography); $k(CH_3O + NO \rightarrow CH_3ONO)/k_2 = 2.03 \pm 0.47$ over range 392–420 K; $k(CH_3O + NO \rightarrow CH_3ONO) = 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200 400 K (CODATA evaluation). k_1/k_2, determined from pyrolysis of CH_3OOCH_3 in presence of NO_2 and N_2, and shown to be pressure dependent.

(e) Static reaction vessel; thermal reaction between NO_2 and C_2H_4 in presence of N_2 at total pressure of 1 atm; relative rate coefficient based on rate of disappearance of NO_2 (spectrophotometry) and end-product analysis (gas chromatography) but no details of calculation given.

(f) The value of k_2 was selected to give the ratio $k(CH_3O + O_2 \rightarrow HCHO + HO_2)/k_2$ consistent with yields of CH_3ONO_2 found in smog chamber experiments.

Preferred Values

$k_2 = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 298–400 K.

Reliability

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

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

Comments on Preferred Values

The preferred value of k_2 is the simple average of the data of Phillips and Shaw,[1] Wiebe *et al.*,[3] and Batt and Rattray,[4] with an assumed zero temperature coefficient. Direct measurements of this rate coefficient would be desirable. Batt and Rattray[4] have shown that the branching ratio k_1/k_2 is pressure dependent but does not exceed the value of 0.05 within the temperature range 380–425 K.

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$CH_3O + O_2 \rightarrow HCHO + HO_2$

$\Delta H^\circ = -112.8$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<2\times10^{-15}$	298	Sanders *et al.*, 1980[1]	(a)
$1.05\times10^{-13}\exp(-1310/T)$	413–628	Gutman, Sanders, and Butler, 1982[2]	(b)
1.3×10^{-15}	298*		
Reviews and Evaluations			
$1.2\times10^{-13}\exp(-1350/T)$	200–300	NASA, 1982[3]	(c)
$1.3\times10^{-13}\exp(-1350/T)$	298–450	CODATA, 1982[4]	(d)
$1.2\times10^{-13}\exp(-1350/T)$	200–300	NASA, 1983[5]	(c)

Comments

(a) CH_3O generated from pulsed 266 nm photolysis of CH_3ONO and $[CH_3O]$ measured by laser induced fluorescence; k measured directly under pseudo-first-order conditions. Arrhenius parameters calculated from k over range 413–628 K and k at 298 K from study of Cox *et al.*[6]

(b) Same experiment procedure as note (a) but with a heated reaction vessel.

(c) Based on data of Gutman, Sanders, and Butler.[2]

(d) Based on data of Cox *et al.*[6]

Preferred Values

$k = 1.3\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.1\times10^{-13}\exp(-1310/T)$ cm^3 molecule^{-1} s^{-1} over range 298–630 K.

Reliability

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

$\Delta (E/R) = {}^{+1000}_{-500}$.

Comments on Preferred Values

The two recent direct studies[1,2] of this reaction are consistent and in good agreement with previous indirect data[6–8] at 400 K. The recommended Arrhenius parameters are those reported by Gutman *et al.*[2]

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$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

$\Delta H^\circ = -59$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.1\pm1)\times10^{-12}\exp[(380\pm250)/T]$	218–365	Simonaitis and Heicklen, 1981[1]	(a)
$(7.7\pm0.9)\times10^{-12}$	296		
$(8.6\pm2.0)\times10^{-12}$	295	Plumb *et al.*, 1981[2]	(b)
Reviews and Evaluations			
$4.2\times10^{-12}\exp(180/T)$	200–300	NASA, 1982[3]	(c)
7.4×10^{-12}	200–300	CODATA, 1982[4]	(d)
$4.2\times10^{-12}\exp(180/T)$	200–300	NASA, 1983[5]	(c)

Comments

(a) Direct study of CH_3O_2 radicals produced from flash photolysis of Cl_2 in presence of CH_4 and O_2; $[CH_3O_2]$ monitored by ultraviolet absorption at 270 nm; k independent of pressure within range 70–600 Torr.

(b) Discharge-flow system; CH_3O_2 generated from $Cl + CH_4/O_2$ reactions and monitored by mass spectrometry.

(c) Average value of the data of Cox and Tyndall,[8] Sander and Watson,[6] Ravishankara *et al.*,[7] Simonaitis and Heicklen,[1] and Plumb *et al.*[2]

(d) Average value of data of Sander and Watson,[6] Ravishankara *et al.*,[7] Plumb *et al.*,[9] and Cox and Tyndall.[8]

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 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 recent data of Simonaitis and Heicklen[1] and of Plumb *et al.*[2] are in good agreement with our previous evaluation.[4] The recommended rate coefficient at 298 K is the average of the data of Sander and Watson,[6] Ravishankara *et al.*,[7] Cox and Tyndall,[8] Plumb *et al.*,[2] and Simonaitis and Heicklen.[1] We have recommended the slight negative temperature dependence of the rate coefficient, obtained[3] by a least-squares analysis of the results of Ravishankara *et al.*[7] and by Simonaitis and Heicklen.[1] Ravishankara *et al.*[7] have shown that the reaction channel leading to NO_2 accounts for at least 80% of the reaction. This result along with the indirect evidence of Pate *et al.*[10] confirms that NO_2 is the major, if not the only, reaction pathway.

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$$\begin{aligned} CH_3O_2 + CH_3O_2 &\rightarrow CH_3OH + HCHO + O_2 && (1)\\ &\rightarrow 2CH_3O + O_2 && (2)\\ &\rightarrow CH_3OOCH_3 + O_2 && (3)\end{aligned}$$

$\Delta H^\circ(1) = -341$ kJ mol^{-1}

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

$\Delta H^\circ(3) = -158$ kJ 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			
$k_1/k_2 = 1.87$ $k_1/k_3 \geqslant 7.7$	297	Niki *et al.*, 1981[1]	(a)
Reviews and Evaluations			
$1.6\times 10^{-13} \exp(220/T)$	200–300	NASA, 1982[2]	(b)
3.7×10^{-13}	298	CODATA, 1982[3]	(c)
$1.6\times 10^{-13} \exp(220/T)$	200–300	NASA, 1983[4]	(b)

Comments

(a) FTIR study of the photo-oxidation of $CH_3N = NCH_3$ and Cl-initiated oxidation of CH_4 at 700 Torr; direct monitoring of products CH_3OH, HCHO, and CH_3O_2H; the ratio k_1/k_3 is based on an upper limit for the detection of CH_3OOCH_3.

(b) k at 298 K is average of data reported by Hochanadel *et al.*,[5] Parkes,[6] Anastasi, Smith, and Parkes,[7] Kan *et al.*,[8] Sanhueza. Simonaitis, and Heicklen,[9] and Sander and Watson[13]; the temperature coefficient is that measured by Sander and Watson.[10]

(c) Recommended k was obtained from data of Kan and Calvert,[11] Sanhueza, Simonaitis, and Heicklen,[9] Kan *et al.*,[8] Cox and Tyndall,[12] Sander and Watson,[10,13] Adachi, Basco, and James,[14] Hochanadel *et al.*,[5] and Parkes.[6]

Preferred Values

$k = 3.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2/k = 0.35$; $k_3/k \leqslant 0.08$ at 298 K.

Reliability

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

$\Delta k_2/k = \pm 0.15$.

$\Delta k_3/k = \pm 0.075$.

Comments on Preferred Values

There have been no further reports either of the total rate coefficient for this reaction or of the temperature coefficient and our previous evaluation still stands.

The FTIR studies of Niki *et al.*,[1] concerning the branching ratios, are in reasonable agreement with the previous findings of Kan, Calvert, and Shaw,[15] and of Parkes.[16] The recommended branching ratios are based on the data of Niki *et al.*,[1] Kan, Calvert, and Shaw,[15] and Parkes.[16]

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$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$

$\Delta H^\circ = -44.9$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.5) \times 10^{-13}$	295	Plumb and Ryan, 1981[1]	(a)
Relative Rate Coefficients			
2.5×10^{-13}	896	Sampson, 1963[2]	(b)
1.4×10^{-13}	713	Baldwin, Walker, and Langford, 1969[3]	(c)
1.3×10^{-13}	813	Baldwin, Pickering, and Walker, 1980[4]	(d)

Comments

(a) Discharge-flow system with He carrier gas; C_2H_5 generated from $Cl + C_2H_6$; $[C_2H_5]$ and $[C_2H_4]$ measured directly by mass spectrometry; rate coefficient $k(C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2)$ determined from yields of C_2H_4; k found to be independent of the pressure (0.6–10 Torr).

(b) Flow system for studying O_2–C_2H_6 thermal reaction with analysis of C_2H_4 product; rate coefficient derived from rate of formation C_2H_4 and calculated $[C_2H_5]$; very indirect determination.

(c) Static reaction system; oxidation of C_2H_5CHO in aged boric acid-coated vessels; relative rate coefficients obtained from end-product analysis of C_2H_4 and C_2H_6; $k/k(C_2H_5 + C_2H_5CHO) = 41$ at 713 K and taking[5] $k(C_2H_5 + C_2H_5CHO) = 3.3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 713 K.

(d) Static reaction system; addition of C_2H_6 to mixtures of 2,2,3,3-tetramethylbutane–O_2 and of H_2–O_2; end-product analysis of C_2H_4, C_2H_4O and n-C_4H_{10}; relative rate coefficient at 813 K, $k/k^{1/2}(2C_2H_5 \rightarrow n\text{-}C_4H_{10}) = 3.2 \times 10^{-8}$ (cm^3 molecule^{-1} s^{-1})$^{1/2}$ and taking[6] $k(2C_2H_5 \rightarrow n\text{-}C_4H_{10}) = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, Arrhenius equation, $k = 1.4 \times 10^{-12} \exp(-1950/T)$ cm^3 molecule^{-1} s^{-1}, obtained from measured k (813 K) and k at 713 K of Baldwin *et al.*,[3] quoted as $k = 9.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} and presumably calculated from $k/k(C_2H_5 + C_2H_5CHO) = 41$ and taking[3] nonreferenced data for $k(C_2H_5 + C_2H_5CHO)$.

Preferred Value

$k = 2\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The first direct measurements of this rate coefficient at room temperature by Plumb and Ryan[1] are in reasonable agreement with earlier indirect studies by Baldwin and coworkers[3,4] at much higher temperatures. Confirmation of the room-temperature rate and measurement of the temperature coefficient are required. In the meantime, we recommend the rate coefficient of Plumb and Ryan[1] with suitably adjusted error limits.

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$C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$

$\Delta H^\circ = -15$ 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			
$(7.5\pm2)\times10^{-29}$[He]	295	Plumb and Ryan, 1981[1]	(a)
7.5×10^{-29}[He]	298	Slagle, Feng, and Gutman, 1984[2]	(b)

Comments

(a) Discharge flow system with carrier gas He, C_2H_5 generated from $Cl + C_2H_6$, C_2H_5, and C_2H_4 followed by mass spectrometer. Measurements at 2×10^{16}–3.4×10^{17} molecule cm^{-3} extrapolated to k_0 and k_∞ with $F_c = 0.85$.

(b) Flow system with mass spectrometric detection, radicals generated by CO_2 laser photolysis; experiments from 294 to 1002 K giving branching ratios for $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ and $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$. Carrier gas He varied between 1.6×10^{16} and 2.4×10^{17} molecule cm^{-3}. Data in agreement with values measured by Plumb and Ryan.[1]

Preferred Value

$k_0 = 2.0\times10^{-28}(T/300)^{-3.8}[N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Value

Calculated rate constants[1] from theory by Troe, 1979,[3] assuming collision efficiencies β_c for N_2 and O_2 which are twice those measured for He. In order to obtain a "reasonable" β_c value of 0.3 for N_2, $\Delta H^\circ \simeq -133$ kJ mol^{-1} had to be used. Measurements for M = N_2 and better information on the heat of formation and frequencies of $C_2H_5O_2$ are required.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.4\pm0.5)\times10^{-12}$	295	Plumb and Ryan, 1981[1]	(a)
4.4×10^{-12}	300	Slagle, Feng, and Gutman, 1984[2]	(b)
Reviews and Evaluations			
6.9×10^{-12}	298	CODATA, 1982[4]	(c)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

(c) Based on the earlier study by Dingledy and Calvert, 1963,[5] indicating no pressure dependence between 4.8 and 103 Torr.

Preferred Value

$k_\infty = 5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over range 200–300 K.

Comments on Preferred Value

The falloff extrapolation from Plumb and Ryan[1] has been slightly changed assuming a higher F_c value of $F_c \simeq 0.7$. Negligible temperature dependence of k_∞ is assumed.

Intermediate Falloff Range

From the preferred k_0 and k_∞ values one obtains $[N_2]_c = 2.5 \times 10^{16}$ molecules cm^{-3}. The given limiting rate coefficients are consistent with $F_c = 0.7$, representation of $F_c = \exp(-T/T^*)$ leads to $T^* \simeq 840$ K.

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$CH_3CO + O_2(+M) \rightarrow CH_3CO_3(+M)$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.4) \times 10^{-12}$	298	McDade, Lenhardt, and Bayes, 1982[1]	(a)
Relative Rate Coefficients			
7.4×10^{-12}	448	Neiman and Feklisov, 1961[2]	(b)
2.5×10^{-12}	309	Pearson, 1963[3]	(c)
4.1×10^{-12}	373	Hoare and Whytock, 1967[4]	(d)
6.2×10^{-12}	423		
2.2×10^{-12}	423	Hoare and Whytock, 1967[5]	(e)
Reviews and Evaluations			
6.8×10^{-12}	300	Demerjian, Kerr, and Calvert, 1974[6]	

Comments

(a) Flow system with CH_3CO generated from pulsed photolysis of CH_3COCH_3 or $CH_3COCH_2COCH_3$; $[CH_3CO]$ monitored by photoionization mass spectrometry and kinetics obtained from pseudo-first-order decays of CH_3CO; pressure range 1–4 Torr.

(b) Steady-state photolysis of $CH_3{}^{14}CHO$ in presence of C_4H_{10} and O_2; relative rate coefficients obtained from yields of CO and CO_2; $k(CH_3CO \rightarrow CH_3 + CO)/k(CH_3CO + O_2) = 9.0 \times 10^{17}$ molecule cm^{-3} at 448 K and $k(CH_3CO + O_2)$ based on $k(CH_3CO \rightarrow CH_3 + CO)/\mathrm{s}^{-1} = 3.2 \times 10^{13} \exp(-8660/T)$.[7]

(c) Steady-state photolysis of CH_3COCH_3 in presence of O_2; relative rate coefficients obtained from Φ_{CO}; $k(CH_3CO \rightarrow CH_3 + CO)/k(CH_3CO + O_2) = 8.67 \times 10^{12}$ molecule cm^{-3} at 309 K and $k(CH_3CO + O_2)$ based on $k(CH_3CO \rightarrow CH_3 + CO)/\mathrm{s}^{-1} = 3.2 \times 10^{13} \exp(-8660/T)$.[7]

(d) Steady-state photolysis of CH_3COCH_3 in presence of O_2; relative rate coefficients obtained from yields of CO and CO_2; $k(CH_3CO \rightarrow CH_3 + CO)/k(CH_3CO + O_2) = 6.5 \times 10^{14}$ molecule cm^{-3} at 373 K and 6.6×10^{15} molecule cm^{-3} at 423 K; $k(CH_3CO + O_2)$ based on $k(CH_3CO \rightarrow CH_3 + CO)/\mathrm{s}^{-1} = 3.2 \times 10^{13} \exp(-8660/T)$.[7]

(e) Steady-state photolysis of $CH_3COC_2H_5$ in presence of O_2; relative rate coefficients obtained from yields of CO and CO_2; $k(CH_3CO \rightarrow CH_3 + CO)/k(CH_3 + O_2) = 1.9 \times 10^{16}$ molecule cm^{-3} at 423 K, $k(CH_3CO + O_2)$ based on $k(CH_3CO \rightarrow CH_3 + CO)/\mathrm{s}^{-1} = 3.2 \times 10^{13} \exp(-8660/T)$.[7]

Preferred Values

$k = 2.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K at 1–4 Torr.

$k_\infty = 5.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

Comments on Preferred Values

The recent direct measurements[1] of this rate coefficient confirm that this is a fast reaction. Some of the earlier indirect studies involving competition with the reaction $CH_3CO \rightarrow CH_3 + CO$ are in substantial agreement with the direct measurement when more recent[7] data are taken for the reference reaction. Confirmation of the directly measured rate coefficient is required. There may be some falloff effects, which have not been accounted for, such that the value at 1 atm is higher than at a few Torr. Comparison with the $C_2H_5 + O_2 \rightarrow C_2H_5O_2$ reaction ($k_\infty = 5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, this evaluation) suggests the preferred value. The value of k at 1 atm is probably close to k_∞.

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$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$

$\Delta H^\circ = -139$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
8.0×10^{-15}	296	Gutman, Sanders, and Butler, 1982[1]	(a)
9.8×10^{-15}	353		
Reviews and Evaluations			
No recommendation		CODATA, 1982[2]	(b)

Comments

(a) C_2H_5 generated from pulsed 266 nm photolysis of C_2H_5ONO and $[C_2H_5O]$ measured by laser induced fluorescence; k measured directly under pseudo-first-order conditions. On the basis of an A factor, estimated from the data for the analogous reaction, $CH_3O + O_2 \rightarrow HCHO + HO_2$, and the measured room-temperature rate coefficient, the following temperature coefficient was calculated; $k = 7.0\ 10^{-14}\exp(-650/T)$ cm^3 molecule^{-1} s^{-1} over range 296–353 K.

(b) Consideration of experimental data of Batt.[3]

Preferred Value

$k = 8.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The first direct studies of this reaction[1] are in accord with data for the analogous reaction $CH_3O + O_2 \rightarrow HCHO + HO_2$. Confirmation of the rate coefficients and any temperature dependence are desirable.

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$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$ (1)
$C_2H_5O_2 + NO(+M) \rightarrow C_2H_5ONO_2(+M)$ (2)

$\Delta H^\circ(1) = -74.5$ 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			
$(2.7\pm0.2)\times10^{-12}$	298	Adachi and Basco, 1979[1]	(a)
$(8.9\pm3.0)\times10^{-12}$	295	Plumb *et al.*, 1982[2]	(b)
Branching Ratios			
$k_1/k \geqslant 0.80$	295	Plumb *et al.*, 1982[2]	(b)
$k_1/k \geqslant 0.99$	299	Atkinson *et al.*, 1982[3]	(c)
Reviews and Evaluations			
7.4×10^{-12}	298	CODATA, 1982[4]	(d)

Comments

(a) $C_2H_5O_2$ generated from flash photolysis of $C_2H_5N=NC_2H_5$ in presence of O_2; $[C_2H_5O_2]$ monitored by ultraviolet absorption at 250 nm; k obtained from pseudo-first-order decay of $[C_2H_5O_2]$ in presence of NO.

(b) Discharge-flow system with mass spectrometric analysis; $C_2H_5O_2$ generated from $Cl + C_2H_6/O_2$ reactions; $C_2H_5O_2^+$ ions could not be detected; k based on complex analysis of rate of formation of NO_2, with account taken of reaction $HO_2 + NO \rightarrow HO + NO_2$; branching ratios based on amount of NO_2 produced.

(c) Smog chamber study of photo-oxidation of C_2H_6 in NO_x–air mixture at atmospheric pressure, reactions initiated by HO generated from photolysis of CH_3ONO; branching ratio determined from gas-chromatographic analysis of

$C_2H_5ONO_2$ (presumed to be formed from the reactions $C_2H_5O_2 + NO + M \rightarrow C_2H_5O_2NO^* \rightarrow C_2H_5ONO_2$) relative to the rate of consumption of C_2H_6.

(d) Based on rate coefficient of the analogous reaction $CH_3O_2 + NO \rightarrow CH_3O + NO_2$.

Preferred Value

$k = 8.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k \geqslant 0.80$.

Reliability

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

Comments on Preferred Values

The discrepancy between the data of Adachi and Basco[1] and of Plumb *et al.*[2] remains unexplained. Since, however, the technique of Adachi and Basco[1] gave a low rate constant for the analogous reaction $CH_3O_2 + NO \rightarrow CH_3O + NO_2$ it seems likely that the results of these authors are in error. It has been suggested[5] that, for the $CH_3O_2 + NO$ system of Adachi and Basco,[1] the formation of CH_3ONO could lead to interference at the wavelength used to measure the CH_3O_2 absorption and hence to a low value of k.

A similar argument can be applied to the data of Adachi and Basco[1] for the $C_2H_5O_2 + NO$ reaction.

Further work is needed on this reaction to confirm the rate coefficient and also to confirm the branching ratio. The branching ratio reported by Atkinson *et al.*[3] assumes that their observed ethyl nitrate product is formed in the reaction sequence $C_2H_5O_2 + NO + M \rightarrow C_2H_5O_2NO^*$, $C_2H_5O_2NO^* \rightarrow C_2H_5ONO_2$. This conclusion requires further confirmation.

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[4]CODATA Task Group on Chemical Kinetics, D. L. Baulch, R. A. Cox, P. J. Crutzen, R. F. Hampson, J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data **11**, 327 (1982).
[5]S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).

$C_2H_5O_2 + NO_2(+M) \rightarrow C_2H_5O_2NO_2(+M)$

$\Delta H^\circ \simeq -80$ kJ mol^{-1}

Rate-coefficient data

No experimental data

Preferred Value

$k_\infty = 5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

Comments on Preferred Value

This value is chosen in agreement with the values for $CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$ and $C_3H_7O_2 + NO_2 \rightarrow C_3H_7O_2NO_2$ of this evaluation. The reaction at 1 atm should be close to the high-pressure limit.

$C_2H_5O_2 + C_2H_5O_2 \rightarrow C_2H_5OH + CH_3CHO + O_2$ (1)

$$\rightarrow 2C_2H_5O + O_2 \quad (2)$$

$$\rightarrow C_2H_5OOC_2H_5 + O_2 \quad (3)$$

$\Delta H^\circ(1) = -417$ kJ mol^{-1}
$\Delta H^\circ(2) = -49$ 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			
$(1 \pm 0.1) \times 10^{-13}$	298	Adachi, Basco, and James, 1979[1]	(a)
Branching Ratios			
$k_1/k_2 = 0.76$ $k_1/k_3 \geqslant 4.6$	298	Niki *et al.*, 1982[2]	(b)

Comments

(a) Flash photolysis of $C_2H_5N = NC_2H_5$ in the presence of O_2 and Ar at total pressures of ~670 Torr; [$C_2H_5O_2$] monitored by absorption spectroscopy; k derived from computer simulation of measured absorbance and kinetic analysis of complex mechanism.

(b) FTIR study of the photo-oxidation of

$C_2H_5N = NC_2H_5$ and Cl-initiated oxidation of C_2H_6 at 700 Torr; direct monitoring of products, CH_3CHO, C_2H_5OH, and $C_2H_5O_2H$; the ratio k_1/k_3 is based on an upper limit for the detection of $C_2H_5OOC_2H_5$.

Preferred Values

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

$k_2/k = 0.52$; $k_3/k \leqslant 0.09$ at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

$\Delta k_2/k = \pm 0.15$.

$\Delta k_3/k = \pm 0.09$.

Comments on Preferred Values

The overall rate coefficient for the interaction of ethylperoxy radicals measured by Adachi, Basco, and James,[1] seems reasonable and is in line with the trend observed in the liquid phase,[3] that the rate coefficient decreases with increasing alkyl substitution in the peroxy radical.

Both the rate coefficient and the branching ratios require further confirmation.

References

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$n\text{-}C_3H_7 + O_2 + M \rightarrow n\text{-}C_3H_7O_2 + M$

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.5 \pm 0.9)\times10^{-12}$ at 1–4 Torr	298	Ruiz and Bayes, 1984[1]	(a)
$\geqslant 3\times10^{-12}$ at 1.5–6 Torr	400	Gutman, 1984[2]	(b)

Comments

(a) Flash photolysis with photoionization mass spectrometer detection of radicals, bath gases He and N_2 at 1–4 Torr. No pressure dependence of k detected. k_∞ between the corresponding values for $C_2H_5 + O_2 \rightarrow C_2H_5O_2$ ($k_\infty = 5\times10^{-12}$ cm^3 molecule^{-1} s^{-1}) and $n\text{-}C_4H_9 + O_2 \rightarrow n\text{-}C_4H_9O_2$ ($k_\infty = 7.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, data for Lenhardt, McDade, and Bayes, 1980[3]).

(b) Flow system with mass-spectrometric detection. Radicals formed by CO_2 laser photolysis. Carrier gases He and N_2 at 1.5–6 Torr. Experiments at 400–635 K showing increasing falloff contributions. Therefore, the value obtained at 400 K should be considered a lower limit.

Preferred Value

$k_\infty = 6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over range 200–300 K.

Comments on Preferred Value

Data from Ruiz and Bayes[1] are chosen. Limited falloff corrections appear necessary.

References

[1] R. P. Ruiz and K. D. Bayes, J. Phys. Chem. **88**, 2592 (1984).
[2] D. Gutman (unpublished work, 1984).
[3] T. M. Lenhardt, E. E. McDade, and K. D. Bayes, J. Chem. Phys. **72**, 304 (1980).

$i\text{-}C_3H_7 + O_2 + M \rightarrow i\text{-}C_3H_7O_2 + M$

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(14.1 \pm 2.4)\times10^{-12}$ at 1–4 Torr	298	Ruiz and Bayes, 1984[1]	(a)

Comments

(a) Flash photolysis with photoionization mass spectrometer detection of radicals, bath gases He and N_2 at 1–4 Torr. No pressure dependence of k detected. k_∞ between the corresponding values for $C_2H_5 + O_2 \rightarrow C_2H_5O_2$ ($k_\infty = 5\times10^{-12}$ cm^3 molecule^{-1} s^{-1}) and $s\text{-}C_4H_9 + O_2 \rightarrow s\text{-}C_4H_9O_2$ ($k_\infty = 16.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1}; data from Lenhardt, McDade, and Bayes, 1980[2]).

Preferred Value

$k_\infty = 1.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over range 200–300 K.

Comments on Preferred Value

The data need confirmation since they are from a single laboratory only.

References

[1] R. P. Ruiz and K. D. Bayes, J. Phys. Chem. **88**, 2592 (1984).
[2] T. M. Lenhardt, E. E. McDade, and K. D. Bayes, J. Chem. Phys. **72**, 304 (1980).

$n\text{-}C_3H_7O_2 + NO \rightarrow C_3H_7O + NO_2$ (1)
$n\text{-}C_3H_7O_2 + NO + M \rightarrow n\text{-}C_3H_7ONO_2 + M$ (2)

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

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Branching Ratios			
$k_2/k = 0.04$	298	Carter *et al.*, 1979[1]	(a)
$k_2/k = 0.036 \pm 0.005$	299	Atkinson *et al.*, 1982[2]	(b)

Comments

(a) Smog chamber experiments. Computer modeling of smog mechanism giving ± 20% agreement with major and ± 30% with minor constituents.

(b) Photolysis of methyl nitrite–NO–*n*-alkane mixtures or of Cl_2–NO–*n*-alkane mixtures at 735 Torr of air. Determination of fraction of alkyl nitrate formation versus NO_2 formation by abstraction.

Preferred Value

$k_2 = 2.9\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and at 1 atm of air.

Reliability

$\Delta \log k_2 = \pm 0.5$ at 298 K and 1 atm of air.

Comments on Preferred Value

The branching ratio measurement by Atkinson *et al.*[2] agrees with that by Carter *et al.*[1] The overall absolute rate coefficient is assumed to be similar to those of the methyl peroxy and the ethyl peroxy reactions with NO.

References

[1] W. P. L. Carter, A. C. Lloyd, J. L. Sprung, and J. N. Pitts, Int. J. Chem. Kinet. **11**, 45 (1979).
[2] R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, J. Phys. Chem. **86**, 4563 (1982).

$i\text{-}C_3H_7O_2 + NO_2 + M \rightarrow i\text{-}C_3H_7O_2NO_2 + M$

High-pressure rate coefficients
Rate coefficient data

k_∞ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.6 \pm 0.2)\times10^{-12}$	298	Adachi and Basco, 1982[1]	(a)

Comments

(a) Flash photolysis with detection of the isopropylperoxy radical via absorption at 265 nm. Mixtures of azoisopropane, O_2, and NO_2 photolyzed at total pressures of 55–400 Torr. No dependence of rate coefficient on total pressure was detected.

Preferred Value

$k_\infty = 5.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ over range 200–300 K.

Comments on Preferred Value

The only available experimental value is in good agreement with the related value for $CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$ from the CODATA evaluation.[2] No major falloff effects are expected above 50 Torr.

References

[1] H. Adachi and N. Basco, Int. J. Chem. Kinet. **14**, 1243 (1982).
[2] CODATA Task Group on Chemical Kinetics, D. L. Baulch, R. A. Cox, P. J. Crutzen, R. F. Hampson, J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data **11**, 327 (1982).

$CH_3CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CH_3CHO + h\nu \rightarrow CH_4 + CO$	(1)	− 25.4	
$\rightarrow CH_3 + HCO$	(2)	341.4	350.1
$\rightarrow CH_3CO + H$	(3)	354.1	337.5

Absorption cross section

Wavelength range/nm	Reference	Comment
290–331.2	Horowitz and Calvert, 1982[1]	

Quantum yield data [$\phi = \phi_1 + \phi_2 + \phi_3$]

Measurement			Wavelength/nm	Reference	Comments
$\phi_1 = 0.063$,	$\phi_2 = 0.887$,	$\phi_3 = 0.076$	290.0	Horowitz and Calvert, 1982[1]	(a)
$\phi_1 = 0.011$,	$\phi_2 = 0.930$,	$\phi_3 = 0.059$	300.0	Horowitz, Kershner, and Calvert, 1982[2]	(a)
$\phi_1 = 0.018$,	$\phi_2 = 0.924$,	$\phi_3 = 0.055$	313.0		(a)
$\phi_1 = 0.079$,	$\phi_2 = 0.470$,	$\phi_3 = 0.00$	320.0		(a)
$\phi_1 = 0.035$,	$\phi_2 = 0.051$,	$\phi_3 = 0.00$	331.2		(a)
$\phi_1 = 0.46$,	$\phi_2 = 0.31$		260	Meyrahn, Moortgat, and Warneck, 1982[3]	(b)
$\phi_1 = 0.42$,	$\phi_2 = 0.32$		265		
$\phi_1 = 0.31$,	$\phi_2 = 0.39$		270		
$\phi_1 = 0.16$,	$\phi_2 = 0.51$		275		
$\phi_1 = 0.05$,	$\phi_2 = 0.58$		280		
$\phi_1 = 0.02$,	$\phi_2 = 0.57$		285		
$\phi_1 = 0.01$,	$\phi_2 = 0.53$		290		
$\phi_1 = 0.005$,	$\phi_2 = 0.48$		295		
$\phi_1 = 0.0$,	$\phi_2 = 0.43$		300		
$\phi_1 = 0.0$,	$\phi_2 = 0.37$,	$\phi_3 = 0.07$	305		
$\phi_1 = 0.0$,	$\phi_2 = 0.28$		310		
		$\phi_3 = 0.05$	313		
$\phi_1 = 0.0$,	$\phi_2 = 0.10$		320		
$\phi_1 = 0.0$,	$\phi_2 = 0.04$		325		
$\phi_1 = 0.0$,	$\phi_2 = 0.00$		330		

Comments

(a) Quantum yields of CH_4, CO, and H_2 determined from the photolysis of CH_3CHO alone and in mixtures with CO_2, i-C_4H_8, and O_2 at 298 K. The quantum yields of the primary processes were shown to be pressure dependent; the tabulated data refer to low pressures.

(b) Quantum yields of CH_4 and CO determined from the photolysis of 100 ppm CH_3CHO in air or N_2 at a total pressure of 1 atm. H_2 was found in trace quantities only and hence ϕ_3 was concluded to be negligible. Quantum yield data based on the assumption that $\phi_1 + \phi_2 + \phi_Q = 1$, where ϕ_Q refers to the quenching reaction $CH_3CHO^* + M \rightarrow CH_3CHO + M$. Quantum yield data at 1 atm pressure were found to be independent of the diluent, N_2, or air. Φ_{CO} both in air and N_2 increased as the total pressure was lowered.

Preferred Values

Absorption cross sections and quantum yields for CH_3CHO photolysis (ϕ_1 and ϕ_2 for 1 atm air).

Wavelength	10^{20} σ/cm^2	ϕ_1	ϕ_2
200	0.77		
210	0.31		
220	<0.1		
240	0.42		
250	1.0		
260	2.0	0.46	0.31
270	3.4	0.31	0.39
280	4.5	0.05	0.58
290	4.9	0.01	0.53
295	4.5	0.0	0.48
300	4.3		0.43
305	3.4		0.37
315	2.1	0.17	
320	1.8	0.10	
325	1.1	0.04	
330	0.69	0.00	
335	0.38		
340	0.15		
345	0.08		

Comments on Preferred Values

The measurements of the absorption cross section reported by Horowitz and Calvert[1] agree well with those given in our previous evaluation[4] and the preferred values are therefore unchanged.

The recent measurements of the quantum yields of the primary processes at atmospheric pressure made by Meyrahn, Moortgat, and Warneck,[3] are in agreement with the values reported by Horowitz and Calvert[1] based on their own work[1,2] at lower pressures and in the presence of CO_2, and on the earlier quantum yield measurements of Weaver *et al.*[5] Horowitz and Calvert[1] also present evidence that primary process (2) occurs from the decay of a vibrationally rich triplet state of the molecule while process (1) occurs from high vibrational levels of the excited singlet state of CH_3CHO.

The values of the photodissociation rates of CH_3CHO in the atmosphere, based on the above values of σ and ϕ, are approximately a factor of 5 lower than those given by Weaver *et al.*[5]

References

[1] A. Horowitz and J. G. Calvert, J. Phys. Chem. **86**, 3105 (1982).

[2] A. Horowitz, C. J. Kershner, and J. G. Calvert, J. Phys. Chem. **86**, 3094 (1982).

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[4] 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).

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4.5. Sulfur Compounds

$O + CH_3SCH_3 \rightarrow CH_3SO + CH_3$

$\Delta H^\circ = -125.6$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.11 \pm 0.12)\times 10^{-11}$ exp[$(460 \pm 41)/T$)]	296–557	Nip, Singleton, and Cvetanovic, 1981[1]	(a)
5.11×10^{-11}	297		
Relative Rate Coefficients			
$(5.51 \pm 0.42)\times 10^{-11}$	298	Nip, Singleton, and Cvetanovic, 1981[1]	(b)
Reviews and Evaluations			
1.3×10^{-11} exp$(390/T)$	270–500	CODATA, 1982[2]	(c)

Comments

(a) Modulated Hg photosensitization of N_2O used as source of $O(^3P)$, which is detected by chemiluminescence with NO. First-order rate constants for phase shift technique in presence of excess CH_3SCH_3.

(b) Product analysis in Hg photosensitization of N_2O–butene–1–CH_3SCH_3 mixtures. Relative to $k\,[O(^3P) + \text{butene-1}] = 4.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1};[3] $k/k\,(O + \text{butene-1}) = 13.8 \pm 0.9$. 95% confidence limits given for k.

(c) Based on data of Lee *et al.*[4,5]

Preferred Values

$k = 5.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3\times10^{-11}\exp(409/T)$ cm^3 molecule^{-1} s^{-1} over 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 new data of Nip *et al.*[1] are in excellent agreement with both studies of Lee *et al.*,[4,5] upon which the previous evaluation was based, over the whole temperature range. The preferred values of k at 298 and (E/R) are obtained from a least-squares fit of the data from those three studies. Recent product studies[6] show that at high pressures 300–1200 Torr, 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).

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[5] J. H. Lee, I. N. Tang, and R. B. Klemm, J. Chem. Phys. **72**, 1793 (1980).

[6] R. J. Cvetanovic, D. L. Singleton, and R. S. Irwin, J. Am. Chem. Soc. **103**, 3530 (1981).

$O + CS_2 \rightarrow SO + CS$ (1)

$$
\begin{aligned}
O + CS_2 &\rightarrow SO + CS \quad (1)\\
&\rightarrow CO + S_2 \quad (2)\\
&\rightarrow OCS + S \quad (3)
\end{aligned}
$$

$\Delta H^\circ(1) = -89$ kJ mol^{-1}

$\Delta H^\circ(2) = -348$ kJ mol^{-1}

$\Delta H^\circ(3) = -231$ 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			
$(3.3 \pm 0.3)\times10^{-12}$	298	Talrose *et al.*, 1978[1]	(a)
Relative Rate Coefficients			
$k_2/k = (0.6 \pm 0.2)\times10^{-2}$	298	Talrose *et al.*, 1978[1]	(a)
$k_3/k = (0.6 \pm 0.2)\times10^{-2}$	298		
Reviews and Evaluations			
$5.8\times10^{-11}\exp(-700/T)$	200–500	CODATA, 1982[2]	(b)
$3.2\times10^{-11}\exp(-650/T)$	200–300	NASA, 1982[3]	(c)
$3.2\times10^{-11}\exp(-650/T)$	200–500	NASA, 1983[4]	(c)

Comments

(a) Diffusion cloud technique; mass spectrometric detection of CS_2 in excess O from discharge. 5–20 Torr pressure.

(b) Based on the work of Westenberg and de Haas,[5] Callear and Hedges,[6] Slagle *et al.*,[7] Wei and Timmons,[8] and Graham and Gutman.[9]

(c) Based on Refs. 5–9 and also work of Callear and Smith[10] and Homann *et al.*[11]

Preferred Values

$k = 3.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.2\times10^{-11}\exp(-650/T)$ cm^3 molecule^{-1} s^{-1} over range 200–500 K.

$k_1/k \geqslant 0.90$ over range 200–500 K.

Reliability

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

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

Comments on Preferred Values

The numerous determinations of k at 298 K cover a range of approximately a factor of 2. The data of Talrose *et al.*[1] supports the lower values, and is in good agreement with the NASA recommended value[4] of $k = 3.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K, which is 50% lower than recommended by CODATA previously.[3] The weight of evidence seems to favor the lower values at 298 K and, at least for the temperature range stated, the slightly lower activation energy favored in the NASA evaluation, the Arrhenius expression from which is adopted here.

The branching ratio k_3/k from Ref. 1 is much lower than earlier measurements of Gutman *et al.*[7,9] and the value of k_2/k is inconsistent with an earlier value reported by Hsu *et al.*[12] At this stage our only recommendation for the branching ratio is that $k_1/k \geqslant 0.90$.

References

[1] 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, edited by N. D. Daly, Adv. Mass Spectrom. 7, 693 (1978).

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[11] K. H. Homann, G. Krome, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **72**, 998 (1968).

[12] D. S. Y. Hsu, W. M. Shaub, T. L. Burks, and M. C. Lin. Chem. Phys. Lett. **44**, 143 (1979).

$O + CH_3SSCH_3 \rightarrow CH_3SO + CH_3S$

$\Delta H^\circ = -141$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.35 \pm 0.70) \times 10^{-11} \exp[(251 \pm 61)/T]$	298–571	Nip, Singleton, and Cvetanovic, 1981[1]	(a)
5.11×10^{-11}	298		
Relative Rate Coefficients			
$(9.82 \pm 0.61) \times 10^{-11}$	298	Nip, Singleton, and Cvetanovic, 1981[1]	(b)
Reviews and Evaluations			
2.1×10^{-11}	270–330	CODATA, 1982[2]	(c)

Comments

(a) Modulated Hg photosensitization of N_2O–$O(^3P)$ detected by chemiluminescence with NO. First-order rate constants from phase shift technique in presence of excess CH_3SSCH_3.

(b) Product analysis in Hg photosensitization of N_2O–butene-1–CH_3SSCH_3 mixtures. Relative to $k[O(^3P) + \text{butene-1}] = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; $k/k(O + \text{butene-1}) = 24.5 \pm 1.5$. 95% confidence limits given for k.

(c) Based on data of Lee and Tang.[4]

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 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.*, are about a factor of 2 lower than the earlier discharge flow–resonance fluorescence study of Lee and Tang,[4] 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 new data[1] with the earlier measurements.[4] The temperature dependence is that from Nip *et al.*. with the A factor adjusted to yield the preferred value at 298 K.

Recent product studies[5] show that at high pressures, 300–1200 Torr, the reaction probably proceeds mainly by addition followed by rapid fragmentation to $CH_3S + CH_3SO$.

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$HO + H_2S \rightarrow H_2O + HS$

$\Delta H^\circ = -114$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.4 \pm 1.3) \times 10^{-12} \exp[(-55 \pm 58)/T]$	244–367	Wine *et al.*, 1981[1]	(a)
$(5.13 \pm 0.57) \times 10^{-12}$	297		
$5.9 \times 10^{-12} \exp(-89/T)$	228–518	Leu and Smith, 1982[2]	(b)
$(3.9 \pm 0.7) \times 10^{-12}$	298		
$(5.11 \pm 0.39) \times 10^{-12}$	228	Michael *et al.*, 1982[3]	(c)
$(4.42 \pm 0.36) \times 10^{-12}$	298		
$(5.57 \pm 0.48) \times 10^{-12}$	437		
$(7.8 \pm 2.6) \times 10^{-12} \exp[(-146 \pm 105)/T]$	239–425	Lin, 1982[4]	(d)
$(4.42 \pm 0.48) \times 10^{-12}$	295		
Reviews and Evaluations			
$1.1 \times 10^{-11} \exp(-225/T)$	250–400	CODATA, 1982[5]	(e)
$5.9 \times 10^{-12} \exp(-65/T)$	200–300	NASA, 1982[6]	(f)
$5.9 \times 10^{-12} \exp(-65/T)$	200–300	NASA, 1983[7]	(f)

Comments

(a) Flash photolysis of H_2O–resonance fluorescence detection of HO. Pressure 40–120 Torr Ar. Pseudo-first-order conditions.

(b) Discharge flow–resonance fluorescence detection of HO under pseudo-first-order conditions 0.75–4.0 Torr. Mass spectrometry used to determine HS and other secondary products and to measure stoichiometry. Alternative expression for temperature dependence of the rate coefficient $k = 2.34 \times 10^{-19} T^{2.5} \exp(725/T)$ cm^3 molecule^{-1} s^{-1} gave a good fit to the data.

(c) Flash photolysis of H_2O–resonance fluorescence detection of HO under pseudo-first-order conditions.

(d) Based on earlier data of Westenberg and de Haas,[7] Perry *et al.*[9]

(e) Based on least-squares fit to data from Refs. 1–3, 8, and Cox and Sheppard.[10]

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 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 new data[1–4] are all in very good agreement with each other and with the earlier data.[9,10] The studies reported in Refs. 2–4 showed a slightly parabolic temperature dependence with a minimum value of k near 300 K. Considering the experimental errors, all other studies are consistent with this non-Arrhenius behavior with the exception of the earlier data[8] which showed a much larger temperature coefficient above 300 K. The non-Arrhenius behavior can be rationalized in two parallel mechanisms for the overall reaction of HO with H_2S.

The preferred value at 298 K and the Arrhenius expression are obtained from a least-squares fit of the data from 200–300 K given in Refs. 1–4, 8, and 9. An alternative expression describing the parabolic temperature dependence can be used for 200–520 K: $k = 2.69 \times 10^{-19} T^{2.5} \exp(725/T)$ cm^3 molecule^{-1} s^{-1}. Ths is the expression given by Leu and Smith[2] but with the preexponential factor adjusted to give the preferred 298 K value.

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$HO + CH_3SCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.8 \pm 1.1)\times 10^{-12} \exp[(-138 \pm 46)T]$	248–363	Wine *et al.*, 1981[1]	(a)
$(4.26 \pm 0.56)\times 10^{-12}$	298		
$(9.2 \pm 0.6)\times 10^{-12}$	393	MacLeod, Poulet, and Le Bras, 1983[2]	(b)
$(7.8 \pm 1.0)\times 10^{-12}$	593		
Reviews and Evaluations			
$5.5\times 10^{-12} \exp(150/T)$	200–500	CODATA, 1982[3]	(c)

Comments

(a) Flash photolysis–resonance fluorescence detection of HO. Pseudo-first-order kinetics. 50 Torr pressure.

(b) Discharge flow–EPR detection of HO. 1 Torr pressure.

(c) Based on data of Kurylo,[4] Atkinson *et al.*,[5] and Cox and Sheppard.[6]

Preferred Value

$k = 7.8\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The new data[1] disagrees with the earlier body of data on which the previous recommendation[2] was based, inasmuch as k at 298 K is a factor of 2 lower and the rate exhibits a positive rather than a negative temperature coefficient. On the other hand, the new EPR data[2] at higher temperature appear to support the earlier measurements. The study reported in Ref. 1 appears to be the most rigorous in excluding possible sources of error. Possible sources of error in earlier work are (a) impure reagents, (b) use of wider band vacuum uv flashlamps in the flash photolysis experiments,[4,5] and (c) the possible interference by $O(^3P)$ reaction in the relative rate study,[6] all leading to higher apparent values of k.

In view of the uncertainties in the measurements and the contradiction of the reported values of k we are unable to recommend an expression for the temperature dependence of this reaction. The preferred value at 298 K is a mean of values from Refs. 1 and 4–6 with error limits covering all the values.

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$HO + CS_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leqslant 7\times 10^{-15}$	298	Leu and Smith, 1982[1]	(a)
$\leqslant 3\times 10^{-15}$	520		
$\leqslant 5\times 10^{-14}$	298	Biermann, Harris, and Pitts, 1982[2]	(b)
Relative Rate Coefficients			
$(1.7 \pm 0.9)\times 10^{-12}$(1 atm air)	298	Jones *et al.*, 1982[3]	(c)
$< 10^{-14}$ $(O_2 = 0)$	298		
$(2.7 \pm 0.6)\times 10^{-12}$(1 atm air)	293	Barnes *et al.*, 1983[4]	(d)
$(1.93 \pm 0.13)\times 10^{-12}$ $\left.\begin{matrix} O_2 = 100\ \text{Torr} \\ N_2 = 100\ \text{Torr} \end{matrix}\right\}$	293		
$(4.01 \pm 0.74)\times 10^{-12}$	278		
$(5.57 \pm 0.45)\times 10^{-12}$	264		
$< 5\times 10^{-13}$ $(O_2 = 0)$	293		
Reviews and Evaluations			
$< 1.5\times 10^{-15}$	298	CODATA, 1982[5]	(e)
$< 1.5\times 10^{-15}$	298	NASA, 1982[6]	(f)
$2.0\times 10^{-18} \exp(2200/T)\times P$/Torr	220–298	NASA, 1983[7]	(g)

Comments

(a) Discharge flow–resonance fluorescence detection of HO and mass spectrometric detection of products. Measured values of k at 298 and 530 K were $(4 \pm 3)\times 10^{-15}$ and $(2.1 \pm 0.7)\times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, respectively, but heterogeneous components may have been present and therefore only upper limits are quoted. OCS and SO_2 were detected as products. CS_2OH ($m/e = 93$) was not detected.

(b) Discharge flow–photoionization mass spectrometric detection of CS_2 in the presence of known amounts of HO produced by $H + NO_2$ reactions.

(c) Photolysis of $HONO–CS_2–N_2–O_2$ mixtures at 1 atm. CS_2, OCS, and SO_2 measured; k relative to $k(OH + HONO) = 6.6\times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[8] Overall rate coefficient dependent on $[O_2]$ increasing from $< 10^{-14}$ cm^3 molecule^{-1} s^{-1} at $[O_2] = 0$ to 2.1×10^{-12} cm^3 molecule^{-1} s^{-1} at $[O_2] = 380$ Torr. Reaction products OCS and SO_2 in equal amounts.

(d) HO generated by photolysis of $CH_3ONO–O_2$ mixtures and thermal decomposition HO_2NO_2 in presence of NO. CS_2, OCS, and SO_2 measured. k relative to $k(HO + n\text{-}C_4H_{10}) = 1.76\times 10^{-11} \exp(-570/T)$ cm^3 molecule^{-1} s^{-1}.[9] k found to increase with $[O_2]$, decrease with increasing temperature $[E/R \approx -(2000 \pm 800)\text{K}]$, and increase with total pressure at constant $[O_2]$. Reaction products OCS and SO_2 in equal amounts.

(e) Based on "low" values of Wine *et al.*[10] and Subramonia-Iyer and Rowland.[11]

(f) Based on data of Wine *et al.*[10]

(g) Expression based on data of Jones *et al.*[3] and Barnes *et al.*[4] Multiplying factor P = total pressure (in Torr) of an $N_2 + O_2$ mixture containing 0.2 mole fraction O_2. Recommended value in absence of O_2 was unchanged from previous NASA evaluation.[6]

Preferred Values

$k = < 7.0\times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K; $[O_2] = 0$.

$k = 2.0\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K; 1 atm air.

$k = 8.8\times 10^{-16} \exp(+2300/T)$ cm^3 molecule^{-1} s^{-1} over range 260–300 K in 1 atm air.

Reliability

$\Delta \log k$ (1 atm air) $= \pm 0.3$ at 298 K.

$\Delta (E/R)$ (1 atm air) $= \pm 500$ K.

Comments on Preferred Values

The new results from the relative rate studies[3,4] demonstrate the pronounced effect of O_2 on the overall rate of the $HO_3 + CS_2$ reaction. The temperature and pressure dependences reported on Ref. 4 support the suggestion[3] that reaction proceeds by addition followed by reaction of the adduct with O_2. The results from the flow systems[1,2] confirm that reaction is very slow in the absence of O_2 and the apparent negative temperature dependence in the measured rates in Ref. 1 and also in the earlier flash photolysis study of Wine *et al.*[10] support an addition mechanism.

The preferred value in the absence of O_2 is the upper limit given in Ref. 1. In air at 1 atm, the recommendations are based on the mean of the 295 and 293 K values from Refs. 3 and 4, respectively, $(2.2\times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, 294 K) and the temperature dependence for $O_2 = 100$ Torr (total pressure = 700 Torr), $E/R = 2300$ K, based on the data of Barnes *et al.*[4]

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$HO + CH_3SSCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.9 \pm 3.3)\times 10^{-11} \exp(+380 \pm 160/T)$ $(1.98 \pm 0.18)\times 10^{-10}$	249–367 298	Wine *et al.*, 1981[1]	(a)
Reviews and Evaluations			
2.2×10^{-10}	298	CODATA, 1982[2]	(b)

Comments

(a) Flash photolysis–resonance fluorescence study. 50–200 Torr Ar.

(b) Based on relative rate study of Cox and Sheppard[3] at room temperature.

Preferred Values

$k = 2.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.0 \times 10^{-11} \exp(380/T)$ cm^3 molecule^{-1} s^{-1} over range 250–370 K.

Reliability

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

$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The new direct determinations of k^1 are in excellent agreement with the earlier room-temperature relative rate determination.[3] The preferred value at 298 K is a mean of all individual determinations at 298 (4 from Ref. 1, 1 from Ref. 3). The temperature dependence from Ref. 1 is accepted with the A factor adjusted to give the preferred value at 298 K. The negative temperature dependences provides further support that the reaction proceeds via addition to the S–S linkage.

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HO + OCS→products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.3 \pm 0.3) \times 10^{-12} \exp[-(2300 \pm 100)/T]$	300–520	Leu and Smith, 1981[1]	(a)
6×10^{-16}	298		
Reviews and Evaluations			
$< 9 \times 10^{-15}$	298	CODATA, 1982[2]	(b)
$1.3 \times 10^{-12} \exp(-2300/T)$	200–400	NASA, 1983[3]	(c)
$1.3 \times 10^{-12} \exp(-2300/T)$	200–300	NASA, 1983[4]	(c)

Comments

(a) Discharge flow–resonance fluorescence detection of HO and product identification by mass spectrometry. Special precautions taken to remove H_2S impurities. HS detected as primary product, HSO and SO_2 as secondary products. Adduct OCS(OH) (m/l 77) not found.

(b) Based on work of Ravishankara *et al.*[5]

(c) Based on data of Leu and Smith.[1]

Preferred Values

$k = 6 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3 \times 10^{-12} \exp(-2300/T)$ cm^3 molecule^{-1} s^{-1} over range 200–520 K.

Reliability

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

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

Comments on Preferred Values

The new data are about a factor of 10 lower than those from Ref. 4 obtained by flash photolysis, which formed the basis of our previous evaluation. The discharge flow technique should be superior for this reaction, since it avoids the problems of photodissociation of the OCS inherent in flash photolysis. However, the most likely cause of the discrepancy is considered[1] to be the pressure of H_2S impurity in the OCS employed in the earlier study. The preferred values are based on the results of Leu and Smith.[1]

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$HO + SO_2 + M \rightarrow HOSO_2 + M$

$\Delta H^\circ = -223$ 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			
$(2.54 \pm 0.33) \times 10^{-31}$ [N_2]	298	Leu, 1982[1]	(a)
$(2.46 \pm 0.32) \times 10^{-31}$ [O_2]			
$(7.91 \pm 0.24) \times 10^{-32}(T/298)^{-2.85+0.21}$ [He]	261–414		
1.6×10^{-31} [N_2]	297	Paraskevopoulos, Singleton, and Irwin, 1983[2]	(b)
$5.0 \times 10^{-31}(T/300)^{-3.3}$ [N_2]	298	Wine *et al.*, 1984[3]	(c)
Reviews and Evaluations			
$3.0 \times 10^{-31}(T/300)^{-2.9}$ [N_2]	200–400	CODATA, 1982[4]	(d)
$3.0 \times 10^{-31}(T/300)^{-2.9}$ [air]	200–300	NASA, 1982[5]	(e)
$3.0 \times 10^{-31}(T/300)^{-3.4}$ [air]	200–300	NASA, 1983[6]	(f)

Comments

(a) Discharge flow–resonance fluorescence technique, pressures around 1 Torr. Relative efficiencies of M, N_2: O_2: He: Ar: CO_2: SO_2 = 1.00:0.97:0.31:0.43:4.7:4.5. Temperature coefficients for M = SO_2:$k_0 \propto (T/298)^{-2.78}$ (pressure range 0.02–0.2 Torr).

(b) Flash photolysis of N_2O–H_2 mixtures, HO detection by resonance absorption. Pressure range 55–760 Torr. Falloff extrapolation using Lindemann–Hinshelwood expression may be responsible for low value.

(c) Flash photolysis–resonance fluorescence technique. Temperature range 260–420 K, pressure range 13–696 Torr, bath gases He, Ar, N_2, and SF_6. Measurements in the falloff region of the reaction, extrapolation to the low-pressure limit using theoretical falloff expressions from Troe, 1979.[7]

(d) Following evaluation by Zellner, 1978.[8]

(e) Following CODATA, 1982.[4]

(f) Following CODATA, 1982.[4] Minor changes in the temperature coefficient calculated by Patrick and Golden.[9]

Preferred Value

$k_0 = 5.0 \times 10^{-31}(T/300)^{-3.3}$ [N_2] cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

$\Delta n = \pm 0.5$.

Comments on Preferred Value

The new but still unpublished values by Wine *et al.*[3] suggest that Leu's[4] measurements have been made in the falloff range such that a small value for k_0 was derived. The theoretical evaluation of the new data leads to values of k_0, k_∞, and F_c which reproduce the low-pressure measurements by Leu[4] reasonably well. Although the data by Wine are unpublished and may be subject to further revision, we feel that the earlier k_0 values have to be revised. For tropospheric conditions, the new data appear to be lower than earlier measurements by 10% to 30%. Because of the particularly careful experiments and evaluation, we prefer the new data.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.2×10^{-12}	297	Paraskevopoulos, Singleton, and Irwin, 1983[2]	(a)
$1.3 \times 10^{-12}(T/300)^{-1.2}$	260–420	Wine *et al.*, 1984[3]	(b)
Reviews and Evaluations			
2×10^{-12}	200–400	CODATA, 1982[4]	(c)
2×10^{-12}	200–300	NASA, 1982[5]	(d)
2×10^{-12}	200–300	NASA, 1983[6]	(d)

Comments

(a) See comment (b) for k_0. A Lindemann–Hinshelwood extrapolation was used which may have led to unreliable high-pressure limiting rate coefficients.

(b) See comment (c) for k_0. The negative temperature coefficient from the falloff extrapolation may indicate that k_∞ is still higher.

(c) See comment (d) for k_0.

(d) See comment (e) for k_0.

Preferred Value

$k_\infty = 2\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over range 200–300 K.

Comments on Preferred Value

More reliable values of k_∞ apparently can only be obtained by measurements at pressures above 1 atm.

Intermediate Falloff Range

The theoretical evaluation of the falloff curves from the measurements by Wine *et al.*, 1984[3] leads to $F_c = 0.45$ at 300 K. Represented as $F_c = \exp(-T/T^*)$, this corresponds to $T^* = 380$ K. Although for internal consistency k_0, k_∞, and F_c values from one evaluation should be used, we feel that the k_∞ value from Wine *et al.*, 1984[3] should be revised up.

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$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3$ (1)
$\rightarrow CH_3O_2SO_2$ (2)

$\Delta H^\circ(1) = -92$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$k_1 \leqslant 1\times 10^{-16}$ $k_2 = (1.4\pm 0.2)\times 10^{-14}$	298	Kan, Calvert, and Shaw, 1981[1]	(a)
Reviews and Evaluations			
$\leqslant 5\times 10^{-17}$	298	CODATA, 1982[2]	(b)
$\leqslant 5\times 10^{-17}$	298	NASA, 1982,[3] 1983[4]	(c)

Comments

(a) Product analysis by FTIR spectroscopy in the photolysis of azomethane–O_2–SO_2 mixtures. Complex mechanism proposed involving reversible addition of CH_3O_2 to SO_2 in reaction (2). k values dependent on several other reaction rates but effectively relative to k ($CH_3O_2 + CH_3O_2$). Adduct formed in reaction (2) was trapped by reaction with NO produced *in situ* from CH_3ONO photolysis. The high overall rate coefficient observed previously[5,6] is probably due to reaction of the adduct, $CH_3O_2SO_2$, with other radicals present.

(b) Based on results of Sander and Watson.[7]

(c) Based on results in Refs. 1 and 7.

Preferred Value

$k_1 \leqslant 5\times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

k_2 no recommendation.

Comments on Preferred Values

The preferred value is the upper limit given by Sander and Watson.[6] The new data[1] may go some way to reconciling the earlier flash photolysis results obtained at high flash energies[4,5] which gave values for k_1 a factor of 100 higher than the upper limit reported in Ref. 6.

References

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HS + O_2→products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leqslant 3.2 \times 10^{-15}$	298	Tiee *et al.*, 1981[1]	(a)
Reviews and Evaluations			
No recommendation		CODATA, 1982[2]	
$< 3.2 \times 10^{-15}$	298	NASA, 1982,[3] 1983[4]	(b)

Comments

(a) Laser flash photolysis of H_2S laser induced fluorescence detection of HS. Upper limit estimated from analysis of nonexponential decay curves of HS.

(b) Based on results from Ref. 1.

Preferred Value

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

Comments on Preferred Value

The single direct study of this reaction shows that it is very slow at ambient temperature. The upper limit for k is a factor of 100 lower than an earlier upper limit estimate of Cupitt and Glass.[4] HO and SO are the normally formulated reaction products but addition of HS to O_2 is also possible.

References

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HS + NO→products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
5.6×10^{-13}	298	Tiee *et al.*, 1981[1]	(a)
Relative Rate Coefficients			
1.0×10^{-12}	298	Bradley *et al.*, 1973[2]	(b)
Reviews and Evaluations			
6.3×10^{-13}	298	Baulch *et al.*, 1976[3]	(c)

Comments

(a) Laser flash photolysis of H_2S; HS detected by laser induced fluorescence. Pressure = 10 Torr Ar. Pseudo-first-order decay of HS in excess NO.

(b) Discharge flow–ESR detection of HS produced in $H + H_2S$ reaction. Effect of added NO gave ratio $k/k(H + HS) = 2.5 \times 10^{-2}$. Absolute value of k based on $k(H + HS) = 4.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} obtained in the same study. $P = 1.3$ Torr.

(c) Based on work of Bradley *et al.*,[2] but using their own recommendation for $k(H + HS) = 2.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Preferred Value

$k = 5.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

Both the absolute and relative determinations of k are in good agreement when the Baulch *et al.*. value[3] for the reference reaction is employed. The direct study[1] was only reported briefly but appears to be free of complication. The preferred value is a mean of the value given in Refs. 1 and 3. At present there is no information on the reaction products or mechanism.

References

[1] J. J. Tiee, F. B. Wampler, R. C. Oldenbourg, and W. W. Rice, Chem. Phys. Lett. **82**, 80 (1981).

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$SO + O_2 \rightarrow SO_2 + O$

$\Delta H^\circ = -52.6$ kJ mol^{-1}

Rate coefficient data

k /cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.07 \pm 0.16)\times 10^{-16}$	298	Black, Sharpless, and Slanger, 1982[1]	(a)
$(2.4^{+2.6}_{-0.9})\times 10^{-13} \exp[(-2370^{+200}_{-250})/T]$	230–420	Black, Sharpless, and Slanger, 1982[2]	(a)
8.4×10^{-17}	298		
$(1.00^{+0.46}_{-0.32})\times 10^{-13} \exp[(-2180 \pm 117)/T]$	262–363	Goede and Shurath, 1983[3]	(b)
4.9×10^{-17}	298		
Reviews and Evaluations			
$6\times 10^{-13} \exp(-3300/T)$	300–1000	CODATA, 1982[4]	(c)
9×10^{-18}	298	NASA, 1982[5]	(d)
$2.4\times 10^{-12} \exp(-2370/T)$	200–300	NASA, 1983[6]	(e)

Comments

(a) Laser photolysis of SO_2 at 193 nm—SO detected by chemiluminescence from $SO + O_3$ reaction. Pseudo-first-order decay in excess O_2. Pressure 100–500 Torr O_2 + He.

(b) SO produced from O + OCS in flow system. Controlled admission to static volume where pseudo-first-order decay of SO in excess O_2 followed by $SO + O_3$ chemiluminescence. Total pressure 1–200 m Torr O_2.

(c) Based on high-temperature data of Homann *et al.*

(d) Extrapolation from high-temperature data.[7]

(e) Based on work of Black *et al.*[1,2]

Preferred Values

$k = 6.7\times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$k = 1.4\times 10^{-13} \exp(-2275/T)$ over range 230–420 K.

Reliability

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

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

Comments on Preferred Values

The new data[1-3] are the first measurements of this rate coefficient at room temperature and below. The 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 values are systematically lower than those from Ref. 2 by about 35%, but appear to have less experimental uncertainty at temperatures < 300 K. The previous preferred value was based on an extrapolation of high-temperature data and results in estimates of k at 298 K which are a factor of 10 or more lower than the measured values. 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.

References

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$SO + O_3 \rightarrow SO_2 + O_2$

$\Delta H^\circ = -645$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.06 \pm 0.16) \times 10^{-13}$	298	Black, Sharpless, and Slanger, 1982[1]	(a)
$(4.8^{+1.6}_{-0.8}) \times 10^{-12} \exp[(-1170^{+80}_{-120})/T]$	230–420	Black, Sharpless, and Slanger, 1982[2]	(a)
9.46×10^{-14}	298		
Reviews and Evaluations			
$3.2 \times 10^{-12} \exp(-1100/T)$	220–300	CODATA, 1982[3]	(b)
$3.2 \times 10^{-12} \exp(-1100/T)$	200–300	NASA, 1982[4]	(b)
$3.6 \times 10^{-12} \exp(-1100/T)$	200–300	NASA, 1983[5]	(c)

Comments

(a) Laser flash photolysis of SO_2–O_3 mixtures at 193 nm—SO_2 detection by chemiluminescence from $SO + O_3$ reaction. Excess O_3 determined by uv absorption. Pressure: 200 Torr He.

(b) Based on results of Halstead and Thrush[6] and Robertshaw and Smith.[7]

(c) Averaged data from Refs. 1, 2, 6, and 7.

Preferred Values

$k = 8.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.5 \times 10^{-12} \exp(-1170/T)$ over 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 new data of Black *et al.*[1,2] are in good agreement with the earlier work. The preferred value at 298 K is the simple mean of all four measurements from Refs. 1, 2, 6, and 7. The temperature dependence from Black *et al.*[2] is accepted since this study covered a much larger temperature range than the earlier work,[6] which nevertheless gave a value of E/R within the experimental error of the later study.[2]

References

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$SO + NO_2 \rightarrow SO_2 + NO$

$\Delta H^\circ = -245$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.48 \pm 0.20) \times 10^{-11}$	298	Black *et al.*, 1982[1]	(a)
Reviews and Evaluations			
1.4×10^{-11}	298	CODATA, 1982[2]	(b)
1.4×10^{-11}	298	NASA, 1982,[3] 1983[4]	(c)

Comments

(a) Laser flash photolysis of SO_2—SO detected by chemiluminescence from $SO + O_3$ reaction.

(b) Based on work of Clyne and co-workers.[4,5]

(c) Based on data of Clyne and MacRobert[5] and Black *et al.*[1]

Preferred Value

$k = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The new data agrees well with previous results for this reaction. The preferred value is unchanged from the previous CODATA value but the error limits are reduced. In the absence of experimental information on the temperature dependence of k, no recommendation for E/R can be made.

References

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$CS_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reactions	ΔH_0°/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CS_2 + h\nu \rightarrow CS_2^*$ (1)		>281
$\rightarrow CS + S(^3P)$ (2)	426	281
$\rightarrow CS + S(^1D)$ (3)	537	223

Absorption cross-section data

Wavelength range/nm	Reference	Comment
280–360	Wine, Chameides, and Ravishankara, 1981[1]	(a)
318–330	Wu and Judge, 1981[2]	(b)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comment
$\Phi_{OCS} = 0.012$	281–350	Jones, Cox, and Penkett, 1983[3]	(c)

Comments

(a) Spectral resolution 0.4 nm. $\delta_{\max} \approx 1 \times 10^{-19}$ cm^2 at 320 nm. Temperature variation over range $250 < T < 325$ K produced little change in averaged σ values. 298 K values shown in graphical form.

(b) Spectral resolution 0.06 nm $\sigma_{\max} = 1.1 \times 10^{-19}$ at 321.5 nm. Temperature $= 294$ K. Synchrotron continuum source. Spectrum shown in graphical form.

(c) Quantum yield for OCS formation in overall photooxidation of CS_2 in wavelength region indicated. From steady-state photolysis of low partial pressures of CS_2 in air at 1 atm. $CS_2^* + O_2$ is source of OCS.

Preferred Values

Absorption cross sections at 298 K

λ/nm	$10^{21}\,\sigma$/cm^2	λ/nm	$10^{21}\,\sigma$/cm^2
295	9.6	335	5.3
305	46	345	2.6
315	72	355	0.5
325	48		

Quantum yield.

$\Phi_{OCS} = 1.2 \times 10^{-2}$ for 290–360 nm region in 1 atm air.

Comments on Preferred Values

The new studies confirm the structured nature of the absorption in the near uv band (290–350 nm). Since there is insufficient energy to dissociate CS_2 at $\lambda < 281$ nm the photochemical reaction yielding OCS and SO_2 products, reported by Jones *et al.*[3] and in earlier work,[4,5] must arise from reactions involving excited CS_2 molecules. The quantum yield reported by Jones *et al.*[3] is in good agreement with that estimated for CS_2 photolysis in air at 1 atm by Wine *et al.*[1] from earlier data of Wood and Heicklen[4] (i.e., $\Phi_{OCS} = 0.01$–0.015). The preferred value is based on Ref. 3 but should be considered an upper limit since the observed slow oxidation of CS_2 could have been due at least in part to other mechanisms.

References

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$OCS + h\nu \rightarrow$ products

Primary photochemical transitions

Reactions	ΔH°_0/kJ mol^{-1}	$\lambda_{threshold}$/nm
$OCS + h\nu \rightarrow CO + S(^3P)$ (1)	303	394
$\rightarrow CO + S(^1D)$ (2)	414	288

Absorption cross-section data

Wavelength range/nm	Reference	Comment
200–270	Rudolf and Inn, 1981[1]	(a)
185–300	Molina, Lamb, and Molina, 1981[2]	(b)

Quantum yield data ($\Phi = \Phi_1 + \Phi_2$)

Measurement	Wavelength range/nm	Reference	Comment
$\Phi = 0.72 + 0.08$	214–253.7	Rudolf and Inn, 1981[1]	(c)

Comments

(a) Spectral resolution 0.01 nm. Temperature 297 K and 195 K. $\sigma_{max} = 3.13 \times 10^{-19}$ cm^2 at 223.5 nm and 297 K. *With a decrease in temperature from 297 to 195 K*, σ *in*creased by ~5% at $\lambda < 226$ nm but at $\lambda > 226$ nm σ decreased with cooling. 297 K data were tabulated. Residual absorption at $\lambda < 280$ nm with $\sigma \approx 2 \times 10^{-22}$ cm^2 also reported, extending at least to 300 nm. The results first reported in Turco *et al.*[3]

(b) Spectral resolution 0.2 nm. Temperature 295 and 225 K. Data given in figures and tables showing values averaged over 1 nm and averaged over wavelength intervals generally used in stratospheric photodissociation calculations. $\sigma_{max} = 3.27 \times 10^{-19}$ cm^2 at 223 nm. Temperature effects similar to Ref. 1 and earlier work. The cross sections at $\lambda < 280$ nm are significantly lower than those proposed by Rudolf and Inn.[1]

(c) Quantum yields for CO formation using resonance fluorescence detection of CO in the fourth positive system of CO centered at 172.9 nm. Light sources were deuterium lamp (220, 225.8, and 230 nm), Zn lamp (214 nm) and Hg lamp (253.7 nm) with appropriate filter systems. Temperature = 297 K. Φ independent of λ over this range. Value based on the assumption that all the S atoms produced (^{3}P and ^{1}D) react with OCS to produce CO for which earlier work[4,5] provides support.

Preferred Values

Absorption cross sections at 295 and 225 K

	$10^{21}\,\sigma$/cm^2			$10^{21}\,\sigma$/cm^2	
λ/nm	295 K	225 K	λ/nm	295 K	225 K
			240	81.3	59.3
300	0.0009		235	153.6	123.7
295	0.0023	0.0013	230	243.8	211.8
290	0.0077	0.0035	225	310.4	283.0
285	0.0218	0.0084	220	304.8	287.5
280	0.0543	0.0206	215	241.6	236.2
275	0.1504	0.0607	210	150.8	151.6
270	0.376	0.156	205	82.0	82.5
265	0.960	0.423	200	39.3	39.3
260	2.52	1.16	195	20.2	18.9
255	6.64	3.46	190	39.7	26.8
250	16.5	9.79	185	190.3	135.7
245	38.2	25.1			

Quantum yields. ($\Phi = \Phi_1 + \Phi_2$).

$\Phi = 0.80$ over wavelength region 215–260 nm.

$\Phi_2/\Phi = 0.74$.

Comments on Preferred Values

There is good agreement between all of the recent cross-section data for $\lambda < 280$ nm. 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 preferred overall quantum yield of 0.80 is an average of results of Rudolf and Inn[1] and the earlier work of Sidhu *et al.*[4] which gave slightly higher values

($\Phi_1 + \Phi_2 = 0.9$), with $\Phi_2/\Phi \geqslant 0.72$. Breckenridge and Taube[5] obtained $\Phi_2/\Phi = 0.74 \pm 0.04$ and their results suggest strongly that $S(^3P)$ 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.

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4.6. Fluorine Compounds

$$O(^1D) + COF_2 \rightarrow CO_2 + F_2 \qquad (1)$$

$$\rightarrow O(^3P) + COF_2 \qquad (2)$$

$\Delta H^\circ(1) = -197$ kJ mol^{-1}
$\Delta H^\circ(2) = -190$ 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			
$(4.6 \pm 0.4) \times 10^{-10}$	298	Fletcher and Husain, 1978[1]	(a)
$(7.4 \pm 1.2) \times 10^{-11}$	298	Wine and Ravishankara, 1983[2]	(b)
Relative Rate Coefficients			
4.8×10^{-11}	298	Jayanty, Simonaitis, and Heicklen, 1976[3]	(c)
$k_1 = 3.4 \times 10^{-11}$	298	Atkinson *et al.*, 1976[4]	(d)
Branching Ratios			
$k_2/k = 0.71 \pm 0.07$	298	Wine and Ravishankara, 1983[2]	(b)
Reviews and Evaluations			
8.0×10^{-11}	200–300	NASA, 1982[5]	(e)
7.4×10^{-11}	200–300	NASA, 1983[6]	(f)

Comments

(a) Flow system. $[O(^1D)]$ monitored by time-resolved resonance absorption at 115 nm. Data analysis used modified Beer–Lambert law.

(b) Pulsed laser photolysis of O_3 at 248 nm $[O(^3P)]$ monitored by time-resovled resonance fluorescence. Relative importance of deactivation determined by comparison of $[O(^3P)]$ with N_2 as dominant quencher to that with COF_2 as predominant quencher.

(c) Photolysis of O_3–N_2O–COF_2 mixtures at 254 nm. Rate of formation of N_2 measured. Value of k derived from measured ratio, $k/k\,[O(^1D) + N_2O] = 0.41$ and $k\,[O(^1D) + N_2O] = 1.16 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation). Evidence presented for some chemical reaction.

(d) Photolysis of NO_2 at 229 nm. $[COF_2]$ and $[N_2O]$ monitored by infrared absorption spectroscopy. Value of k_1 derived from measured ratio, $k_1/k\,[O(^1D) + N_2O] = 0.29 \pm 0.04$ and $k\,[O(^1D) + N_2O] = 1.16 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

(e) Based on preliminary report of results of Wine and Ravishankara.

(f) Based on results of Wine and Ravishankara.[2]

Preferred Values

$k_1 = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 5.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.2$.

Comments on Preferred Values

The preferred value for k_1 and k_2 are based on the results reported in the recent study of Wine and Ravishankara, 1983[1] which is much more direct than the other studies. Both the overall rate and the branching ratio reported in this study are accepted. The technique of Fletcher and Husain[1] has given problems in the past for well-studied similar reactions, and the value reported appears unacceptably high.

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$F + O_2 + M \rightarrow FO_2 + M$

$\Delta H^\circ = -66$ 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			
$(1.0 \pm 0.3) \times 10^{-32}[O_2]$	298	Chebotarev, 1979[1]	(a)
Reviews and Evaluations			
$1.6 \times 10^{-32}(T/300)^{-2.5}[N_2]$	220–360	CODATA, 1982[2]	(b)
$1.6 \times 10^{-32}(T/300)^{-2.5}$[air]	200–300	NASA, 1982[3]	(c)
$1.6 \times 10^{-32}(T/300)^{-1.4}$[air]	220–300	NASA, 1983[4]	(d)

Comments

(a) Laser flash photolysis near 200 nm of WF_6–H_2–He mixtures in presence of O_2. Detection of HF infrared absorption using an HF laser as background source. Relative efficiency of M, O_2: Ar = 1.4: 1.0 reported.

(b) Average of data by Zetzsch,[5] Arutyunov *et al.*,[6] Chen *et al.*,[7] and Shamonina and Kotov.[8]

(c) Based on Ref. 2.

(d) Rate coefficient at 300 K based on Ref. 2. Temperature coefficient from calculations by Patrick and Golden[9] which were based on a different ΔH° value.

Preferred Value

$k_0 = 1.3 \times 10^{-32}(T/300)^{-1.4}[N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Value

The preferred value averages the new data with older values. The temperature coefficient is taken from the NASA evaluation.[4]

References

[1] N. F. Chebotarev, Kinet. Katal. 20, 1381 (1979).
[2] CODATA Task Group on Chemical Kinetics, D. L. Baulch, R. A. Cox, P. J. Crutzen, R. F. Hampson, J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data 11, 327 (1982).
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[7] H. L. Chen, D. W. Trainor, R. E. Center, and W. I. Fyfe, J. Chem. Phys. 66, 5513 (1977).
[8] N. F. Shamonina and A. G. Kotov, Kinet. Katal. 20, 233 (1979).
[9] R. Patrick and D. M. Golden, Int. J. Chem. Kinet. 15, 1189 (1983).

$F + H_2O \rightarrow HF + HO$

$\Delta H^\circ = -72.0$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.2 \pm 1.0) \times 10^{-11} \exp[-(400 \pm 70)/T]$ $(1.1 \pm 0.1) \times 10^{-11}$	243–369 300	Walther and Wagner, 1983[1]	(a)
Reviews and Evaluations			
$2.2 \times 10^{-11} \exp(-200/T)$	240–360	CODATA, 1982[2]	(b)
$2.2 \times 10^{-11} \exp(-200/T)$	200–300	NASA, 1982[3]	(b)
$2.2 \times 10^{-11} \exp(-200/T)$	200–300	NASA, 1983[4]	(b)

Comments

(a) Discharge flow–mass spectrometric technique.

(b) Based on quotation in review by Jones and Skolnik[5] of results of Zetzsch.[6]

Preferred Values

$k = 1.1 \times 10^{-11}$ exp cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.2 \times 10^{-11} \exp(-400/T)$ cm^3 molecule^{-1} s^{-1} over range 240–370 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

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

Comments on Preferred Values

The preferred values are the recent results of Walther and Wagner.[1] They are the only published results and are selected in preference to the earlier unpublished results of Zetzsch[6] quoted in the review of Jones and Skolnik.[6]

References

[1] C.-D. Walther and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **87**, 403 (1983).

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$F + NO_2 + M \rightarrow FONO + M$

$\Delta H^\circ = -176$ 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			
$(9.8 \pm 1.6) \times 10^{-31}[N_2]$	295	Fasano and Nogar, 1983[1]	(a)
Reviews and Evaluations			
$1.1 \times 10^{-30}(T/300)^{-2.3}$[air]	200–300	NASA, 1982[2]	(b)
$3.3 \times 10^{-30}(T/300)^{-2.0}$[air]	200–300	NASA, 1983[3]	(b)

Comments

(a) F generated by infrared multiphoton dissociation of SF_6. Detection of IR fluorescence from competitive reaction $F + H_2$. Extrapolation of falloff curve to the limits using $F_c = 0.6$.

(b) Calculated rate coefficient from Patrick and Golden[4] based on a collision efficiency of $\beta_c = 0.3$. It is assumed that FONO is formed more rapidly than FNO_2.

Preferred Values

$k_0 = 1.0 \times 10^{-30}(T/300)^{-2.0}[N_2]$ over range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

Because of the uncertainties in estimated β_c values, we prefer the k_0 value from Fasano and Nogar.[1] The temperature coefficient from the NASA[3] evaluation is accepted.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.2 \pm 0.8) \times 10^{-11}$	295	Fasano and Nogar, 1983[1]	(a)
Reviews and Evaluations			
$1.0 \times 10^{-10}(T/300)^{-1.0}$	200–300	NASA, 1982[2]	(b)
$2.0 \times 10^{-10}(T/300)^{-1.0}$	200–300	NASA, 1983[3]	(b)

Comments

(a) As comment (a) for k_0.

(b) Estimate by analogy to $Cl + NO_2$.

Preferred Value

$k = 2.0\times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.8$ over range 200–300 K.

Comments on Preferred Value

The scatter of the falloff measurements in Ref. 1 is too large to allow for a reasonable extrapolation of the measured values to k_∞. For this reason the estimated NASA[2] value is preferred assuming a large uncertainty. A value of $F_c = 0.6$ is accepted from the calculations of Ref. 1 for the reaction (1).

References

[1] D. M. Fasano and N. S. Nogar, J. Chem. Phys. **78**, 6688 (1983).

[2] NASA Panel for Data Evaluation, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 5*, W. B. DeMore, R. T. Watson, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, M. J. Molina, and A. R. Ravishankara, JPL Publ. 82-57 (1982).

[3] NASA Panel for Data Evaluation, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 6*, W. B. DeMore, M. J. Molina, R. T. Watson, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, and A. R. Ravishankara, JPL Publ. 83-62 (1983).

[4] R. Patrick and D. M. Golden, Int. J. Chem. Kinet. **15**, 1189 (1983).

$F + CH_4 \rightarrow HF + CH_3$

$\Delta H^\circ = -139.0$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.72\pm 0.30)\times 10^{-11}$	298	Fasano and Nogar, 1982[1]	(a)
Reviews and Evaluations			
$3.0\times 10^{-10}\exp(-400/T)$	250–450	CODATA, 1982[2]	(b)
$3.0\times 10^{-10}\exp(-400/T)$	200–300	NASA, 1982[3]	(b)
$3.0\times 10^{-10}\exp(-400/T)$	200–300	NASA, 1983[4]	(b)

Comments

(a) Infrared multiphoton dissociation of SF_6 in mixture of CH_4, D_2, and Ar. First-order decay of [F] monitored by chemiluminescence from either HF or DF. Dependence of decay rate on mixture composition gives values for k and for $k(F + D_2 \rightarrow DF + D)$.

(b) Based on absolute values of Wagner *et al.*,[5] Clyne *et al.*,[6] and Kompa and Wanner,[7] and on relative results of Foon and Reid[8] and Pollock and Jones.[9]

Preferred Values

$k = 8\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.0\times 10^{-10}\exp(-400/T)$ cm^3 molecule^{-1} s^{-1} over range 250–450 K.

Reliability

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

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

Comments on Preferred Values

The preferred value is based on room-temperature results of Clyne *et al.*,[6] Kompa and Wanner,[7] Pollock and Jones,[9] and Fasano and Nogar,[1] the 298–450 K results of Wagner *et al.*[5] and the 253–348 K results of Foon and Reid.[8] Because the previous recommendation[2] was based on results of five studies, inclusion of the new result of Fasano and Nogar[1] (which agrees with the recommendation) in the averaging procedure does not change the preferred value.

References

[1] D. M. Fasano and N. S. Nogar, Chem. Phys. Lett. **92**, 411 (1982).

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

[3] NASA Panel for Data Evaluation, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 5*, W. B. DeMore, R. T. Watson, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, M. J. Molina, and A. R. Ravishankara, JPL Publ. 82-57 (1982).

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$COF_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH/kJ mol^{-1}	$\lambda_{threshold}$/nm
$COF_2 + h\nu \rightarrow CO + F_2$	(1)	518	231
$\rightarrow COF + F$	(2)	539	222
$\rightarrow CO + 2F$	(3)	672	178
$\rightarrow CF_2 + O(^3P)$	(4)	697	172

Absorption cross-section data

Wavelength range/nm	Reference	Comments
186–223.5	Molina and Molina, 1982[1]	(a)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi(CO) \sim 0.25$	206	Molina and Molina, 1982[1]	(a)

Comments

(a) Measured at 298 K. Structured absorption spectrum; values reported are averaged over 500 cm^{-1} intervals. For quantum yield measurements, I_2 resonance lamp used to photolyze mixtures of up to 200 Torr COF_2 in 1 atm CH_4. [CO] measured by FTIR. HF also observed.

Preferred Values

Absorption cross sections for COF_2 photolysis at 298 K.

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$ cm^2
186.0	5.5	205.1	0.69
187.8	4.8	207.3	0.50
189.6	4.2	209.4	0.34
191.4	3.7	211.6	0.23
193.2	3.1	213.9	0.15
195.1	2.6	216.2	0.10
197.0	2.1	218.6	0.06
199.0	1.6	221.0	0.04
201.0	1.3	223.0	0.03
203.0	0.95		

Quantum yields.

No recommendations.

Comments on Preferred Values

The preferred values of the absorption cross sections are those of Molina and Molina.[1] The values tabulated are averaged over 500 cm^{-1} intervals. They are preferred over the unpublished results of Chou *et al.* quoted in the previous evaluation.[2] In view of the preliminary nature of the only reported quantum yield data, no recommendation is made.

References

[1] L. T. Molina and M. J. Molina, Results presented at 182nd National Meeting, American Chemical Society, New York, 1982.

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

4.7. Chlorine Compounds

$O + HCl \rightarrow HO + Cl$

$\Delta H^\circ = +3.4$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.1 \pm 2.4) \times 10^{-12} \exp[-(3160 \pm 184)/T]$	330–600	Singleton and Cvetanovic, 1981[1]	(a)
1.3×10^{-16}	298*		
Reviews and Evaluations			
$1.1 \times 10^{-11} \exp(-3370/T)$	293–718	CODATA, 1982[2]	(b)
$1.0 \times 10^{-11} \exp(-3340/T)$	200–300	NASA, 1982[3]	(c)
$1.0 \times 10^{-11} \exp(-3340/T)$	200–300	NASA, 1983[4]	(c)

Comments

(a) Phase-shift technique. Oxygen atoms produced by modulated Hg photosensitized decomposition of N_2O and monitored by chemiluminescent reaction with NO.

(b) Based on results of Wong and Belles,[5] Brown and Smith,[6] Ravishankara *et al.*,[7] and Hack *et al.*[8]

(c) Based on results of studies cited in comment (b) and also on results of Singleton and Cvetanovic.[1]

Preferred Values

$k = 1.4 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.0 \times 10^{-11} \exp(-3340/T)$ cm^3 molecule^{-1} s^{-1} over range 293–718 K.

Reliability

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

$\Delta (E/R) = \pm 350$ K.

Comments on Preferred Values

The preferred value is based on the results of Wong and Belles[5] (356–630 K), of Brown and Smith[6] (293–440 K), of Ravishankara *et al.*[7] (350–454 K), of Hack *et al.*[8] (293–718 K), and of Singleton and Cvetanovic[1] (330–600 K). Inclusion of the new data of Singleton and Cvetanovic[1] produces only a minor change from the previous CODATA evaluation.[2]

References

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$O + ClO \rightarrow O_2 + Cl$

$\Delta H^\circ = -230$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.0 \pm 1.0) \times 10^{-11} \exp[-(96 \pm 20)/T]$	236–422	Leu, 1984[1]	(a)
$(3.6 \pm 0.7) \times 10^{-11}$	296		
$(4.2 \pm 0.8) \times 10^{-11}$	241–298	Margitan, 1984[2]	(b)
Reviews and Evaluations			
$7.5 \times 10^{-11} \exp(-120/T)$	220–425	CODATA, 1982[3]	(c)
$7.7 \times 10^{-11} \exp(-130/T)$	200–300	NASA, 1982[4]	(c)
$7.7 \times 10^{-11} \exp(-130/T)$	200–300	NASA, 1983[5]	(c)

Comments

(a) Discharge flow system. First-order decay of [O] in excess [ClO] monitored by resonance fluorescence. Three sources of ClO used ($Cl + O_3$, $Cl + Cl_2O$, and $Cl + OClO$); results were independent of ClO source.

(b) Flash photolysis system. Most experiments performed at 10 Torr Ar, some at 30 Torr Ar. First-order decay of [O] in excess [ClO] monitored by resonance fluorescence. ClO produced by Cl(excess) + Cl_2O; ClO dissociated approx. 1% by flash to give O atoms. [ClO] measured downstream by optical absorption and correction of up to 20% made to allow for ClO loss by recombination.

(c) Based on 298 K results of Bemand *et al.*,[6] the 220–426 K results of Clyne and Nip,[7] and the 218–295 K results of Zahniser and Kaufman.[8]

Preferred Values

$k = 4.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.4 \times 10^{-11} \exp(-120/T)$ cm^3 molecule^{-1} s^{-1} over range 220–370 K.

Reliability

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

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

Comments on Preferred Values

Preferred value is based on a least-squares fit to the data below 370 K reported in the recent studies of Leu[1] and Margitan[2] and the earlier studies of Bemand *et al.*,[6] Clyne and Nip,[7] and Zahniser and Kaufman.[8] Values reported in the newer studies are lower than those of earlier studies[6,7] and result in a lowering of the preferred value at room temperature by about 15% from the value recommended previously.[3]

References

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$Cl + H_2 \rightarrow HCl + H$

$\Delta H^\circ = +4.6$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.6 \pm 0.3) \times 10^{-11} \exp[-(2310/T)]$	200–500	Miller and Gordon, 1981[1]	(a)
$(1.5 \pm 0.2) \times 10^{-14}$	298		
$(6.0 \pm 0.5) \times 10^{-11} \exp[-(2470 \pm 100)/T]$	297–425	Kita and Stedman, 1982[2]	(b)
$(1.46 \pm 0.22) \times 10^{-14}$	297		
Reviews and Evaluations			
$4.7 \times 10^{-11} \exp(-2340/T)$	210–1070	CODATA, 1982[3]	(c)
$3.7 \times 10^{-11} \exp(-2300/T)$	200–300	NASA, 1982[4]	(d)
$3.7 \times 10^{-11} \exp(-2300/T)$	200–300	NASA, 1983[5]	(d)

Comments

(a) Flash photolysis–resonance fluorescence technique. Also measured rate coefficients for reverse reaction by same technique and found ratio to agree with equilibrium constant data.

(b) Discharge flow–resonance fluorescence technique. Also measured rate coefficient for reverse reaction by same technique and found ratio to agree with equilibrium constant data.

(c) Based on data by Watson *et al.*,[6] Benson *et al.*,[7] and Steiner and Rideal.[8]

(d) Based on data below 300 K reported by Watson *et al.*,[6] Lee *et al.*,[9] and Miller and Gordon.[1]

Preferred Values

$k = 1.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.7 \times 10^{-11} \exp(-2300/T)$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

$\Delta (E/R) = \pm 200$ 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.*,[6] Lee *et al.*,[9] and Miller and Gordon.[1] The results of these three 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.*,[6] Miller and Gordon,[1] and Kita and Stedman[2] agree with the results of Benson *et al.*[7] and Steiner and Rideal.[8] Results of the new study by Kita and Stedman[2] are in excellent agreement with this recommendation. Note that the two newest studies[1,2] have measured both the forward and reverse rates and have shown that the ratio agrees with equilibrium constant data.

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$Cl + HO_2 \rightarrow HCl + O_2$ (1)
$\rightarrow ClO + HO$ (2)

$\Delta H^\circ(1) = -224\ \mathrm{kJ\ mol^{-1}}$
$\Delta H^\circ = +9\ \mathrm{kJ\ mol^{-1}}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.23 \pm 0.07) \times 10^{-11}$	250–414	Lee and Howard, 1982[1]	(a)
Branching Ratios			
$k_2/k = 1.09 \exp(-478/T)$	250–414	Lee and Howard, 1982[1]	(a)
$k_2/k = 0.21 \pm 0.02$	297		
Reviews and Evaluations			
$k_1 = 4.8 \times 10^{-11}$	274–338	CODATA, 1982[2]	(b)
$k_1 = 1.8 \times 10^{-11} \exp(170/T)$	200–300	NASA, 1982[3]	(c)
$k_2 = 4.1 \times 10^{-11} \exp(-450/T)$	200–300		
$k_1 = 1.8 \times 10^{-11} \exp(170/T)$	200–300	NASA, 1983[4]	(c)
$k_2 = 4.1 \times 10^{-11} \exp(-450/T)$			

Comments

(a) Discharge flow system with laser magnetic resonance detection of HO_2, OH, and ClO. On basis of the overall rate and the temperature-dependent expression for the branching ratio, the authors derived the following expressions for the individual rate coefficients: $k_1 = (1.8 \pm 0.5) \times 10^{-11} \exp[(170 \pm 80)/T]$ and $k_2 = (4.1 \pm 0.8) \times 10^{-11} \exp[-(450 \pm 60)/T]$.

(b) Based on indirect studies of Leu and DeMore,[5] Poulet *et al.*,[6] Burrows *et al.*,[7] and Cox.[8]

(c) Based on direct study of Lee and Howard.[1]

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 range 250–420 K.

$k_2 = 4.1 \times 10^{-11} \exp(-450/T)$ cm^3 molecule^{-1} s^{-1} over 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 preferred values for k_1 and k_2 are based on results of the recent direct study by Lee and Howard.[1] These expressions were derived by the authors from data on the overall rate and the branching ratio. The total rate constant is temperature independent with a value of $(4.2 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 250–420 K. The contribution of reaction channel 2 (21% at 298 K) is much higher than estimated previously.[7] The value of k_2 when combined with the value of k ($ClO + OH \rightarrow CL + HO_2$) gives an equilibrium constant value of 1.0 which in turn gives a value for the heat of formation of HO_2 at 298 K of 13.8 kJ mol^{-1} in reasonably good agreement with the value of 10.5 kJ mol^{-1} from Howard[9] (see also review by Shum and Benson.[10])

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$Cl + H_2CO \rightarrow HCl + HCO$

$\Delta H^\circ = -67.4$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(6.6 \pm 1.4) \times 10^{-11}$	298	Poulet, Laverdet, and LeBras, 1981[1]	(a)
Reviews and Evaluations			
$7.9 \times 10^{-11} \exp(-34/T)$	200–500	CODATA, 1982[2]	(b)
$8.2 \times 10^{-11} \exp(-34/T)$	200–300	NASA, 1982[3]	(c)
$8.2 \times 10^{-11} \exp(-34/T)$	200–300	NASA, 1983[4]	(c)

Comments

(a) Discharge flow–mass spectrometric study. Value of k derived from measured ratio $k/k(Cl + C_2H_6) = 1.16$ and $k(Cl + C_2H_6) = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

(b) Based on studies as a function of temperature by Michael *et al.*,[5] and Anderson and Kurylo[6] and room-temperature results of Niki *et al.*[7] and Fasano and Nogar.[8]

(c) Based on all references in (b) and also on Poulet *et al.*[1]

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 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.*[5] and the 223–323 K data of Anderson and Kurylo.[6] The preferred value of k at 298 K is based on of these studies and also the room-temperature results of Niki *et al.*,[7] Fasano and Nogar,[8] and Poulet *et al.*,[1] all of which are in good agreement.

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$Cl + HONO_2 \rightarrow HCl + NO_3$

$\Delta H^\circ = -8.2$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.4 \pm 1.6) \times 10^{-14}$	298	Clark, Husain, and Jezequel, 1982[1]	(a)
$(5.1 \pm 2.8) \times 10^{-12} \exp[-(1700 \pm 150)/T]$	243–298	Kurylo, Knable, and Murphy, 1983[2]	(b)
$(1.67^{+0.21}_{-0.52}) \times 10^{-14}$	298		
Reviews and Evaluations			
$< 7 \times 10^{-15}$	298	CODATA, 1982[3]	(c)
$< 1 \times 10^{-11} \exp(-2170/T)$	200–300	NASA, 1982[4]	(d)
$< 1.7 \times 10^{-14}$	298	NASA, 1983[5]	(e)

Comments

(a) Cl produced by repetitive pulsed photolysis of Cl_2. First-order decay of [Cl] monitored by time-resolved resonance absorption at 139 nm.

(b) Flash photolysis of CCl_4. First-order decay of [Cl] monitored by resonance fluorescence.

(c) Based on assuming that the room-temperature value of Leu and DeMore[6] represents an upper limit.

(d) Based on assuming that the room-temperature value of Leu and DeMore[6] represents an upper limit. The preexponential factor was estimated and the E/R value derived to fit this upper limit at 298 K.

(e) Based on assuming that the room-temperature value of Kurylo *et al.*[2] represents an upper limit.

Preferred Values

$k < 1.7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The two new studies[1,2] which monitored [Cl] decay report values higher than those obtained in discharge flow-mass spectrometric studies by Leu and DeMore[6] and by Poulet *et al.*[7] which monitored [HNO_3] decay. The value of E/R reported by Kurylo *et al.*[2] (1700 K) for 243–298 K is significantly lower than the value reported by Poulet *et al.*[7] (4380 K) for 439–633 K. The data of Poulet *et al.*[7] are not directly applicable to stratospheric conditions and extrapolation to room temperature may not be valid. The preferred value is based on assuming that the 298 K data of Kurylo *et al.*[2] represents an upper limit. The higher value reported by Clark *et al.*[1] is based on data which exhibit significant scatter and is not considered in deriving the preferred value.

References

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$Cl + CH_3CCl_3 \rightarrow HCl + CH_2CCl_3$

$\Delta H^\circ = -27$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$< 2.4 \times 10^{-14}$	259	Wine, Semmes, and Ravishankara, 1982[1]	(a)
$< 3.7 \times 10^{-14}$	298		
Reviews and Evaluations			
$< 4 \times 10^{-14}$	298	NASA, 1983[2]	(b)

Comments

(a) Pulsed laser photolysis of Cl_2. First-order decay of [Cl] monitored by resonance fluorescence. Experiments also performed at 356 and 403 K. Nonexponential decay observed at 403 K. Authors concluded that the presence of a reactive impurity accounted for a significant fraction of the [Cl] decay, and therefore reported only upper limits for k.

(b) Based on results of Wine *et al.*[1]

Preferred Values

$k < 4 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Comments on Preferred Values

Preferred value is based on the only reported study[1] of this reaction. The observed decay rate includes a significant contribution from a reactive impurity and therefore only an upper limit for k can be derived. This reaction is too slow to be of importance in atmospheric chemistry.

References

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$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$

$\Delta H^\circ = -77$ kJ mol^{-1}

Rate coefficient data

k /cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.3 \times 10^{-12} \exp(150/T)$	219–298	Margitan, 1983[1]	(a)
$(1.04 \pm 0.04) \times 10^{-11}$	298		
$7.3 \times 10^{-12} \exp(165/T)$	220–296	Kurylo, Knable, and Murphy, 1983[2]	(b)
$(1.20 \pm 0.24) \times 10^{-11}$	296		
Reviews and Evaluations			
$1.7 \times 10^{-12} \exp(-610/T)$	224–273	CODATA, 1982[3]	(c)
$6.0 \times 10^{-12} \exp(150/T)$	200–300	NASA, 1982[4]	(d)
$6.8 \times 10^{-12} \exp(160/T)$	200–300	NASA, 1983[5]	(e)

Comments

(a) Flash photolysis of Cl_2 at 355 nm. First-order decay of [Cl] monitored by resonance fluorescence. O-atom abstraction channel to give $ClO + ClONO$ shown to be unimportant based on results of experiments with added NO, in which Cl was not regenerated by the fast reaction $ClO + NO \rightarrow Cl + NO_2$.

(b) Flash photolysis of CCl_4 or $COCl_2$. First-order decay of [Cl] monitored by resonance fluorescence. Results supersede earlier results[6] from same laboratory.

(c) Based on results of Kurylo and Manning.[6]

(d) Based on results of Margitan.[1]

(e) Based on results of Margitan[1] and Kurylo *et al.*[2]

Preferred Values

$k = 1.2 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$k = 6.8 \times 10^{-12} \exp(160/T)$ cm^3 $molecule^{-1}$ s^{-1} over range 219–298 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.

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

Comments on Preferred Values

The preferred value averages the recent results of Margitan[1] and Kurylo *et al.*[2] which are in good agreement. These results show that the rate constant for this reaction is two orders of magnitude greater than was indicated by the only earlier published study.[6] In that study it now seems likely that the reaction actually being observed was the slower reaction $O + ClONO_2$. Margitan[1] has shown that the reaction proceeds by Cl atom abstraction rather than by O atom abstraction.

References

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$HO + HCl \rightarrow H_2O + Cl$

$\Delta H^\circ = -67.4$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.66 \pm 0.52)\times 10^{-13}$	300	Husain, Plane, and Slater, 1981[1]	(a)
Reviews and Evaluations			
$3.0\times 10^{-12}\exp(-425/T)$	210–460	CODATA, 1982[2]	(b)
$2.8\times 10^{-12}\exp(-425/T)$	200–300	NASA, 1982[3]	(c)
$2.8\times 10^{-12}\exp(-425/T)$	200–300	NASA, 1983[4]	(c)

Comments

(a) Flash photolysis. First-order decay of [HO] monitored by resonance fluorescence.

(b) Based on results reported by Takacs and Glass,[5] Zahniser *et al.*,[6] Smith and Zellner,[7] Ravishankara *et al.*,[8] and Hack *et al.*[9]

(c) Based on results in (b) and in Husain *et al.*[1]

Preferred Values

$k = 6.6\times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.8\times 10^{-12}\exp(-425/T)$ cm^3 molecule^{-1} s^{-1} over range 210–460 K.

Reliability

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

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

Comments on Preferred Values

There is good agreement between the room-temperature values reported in six studies[1,5–9] and the preferred value is the average of the six values. The Arrhenius expression was derived by giving equal weighting to the temperature-dependent data reported in Refs. 6–8.

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$HO + ClO \rightarrow HO_2 + Cl$ (1)
$\rightarrow HCl + O_2$ (2)

$\Delta H^\circ(1) = -9$ kJ mol^{-1}

$\Delta H^\circ(2) = -234$ 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			
$(1.17 \pm 0.33)\times 10^{-11}$	248–335	Ravishankara, Eisele, and Wine, 1983[1]	(a)
Reviews and Evaluations			
9.1×10^{-12}	298	CODATA, 1982[2]	(b)
$5.1\times 10^{-12}\exp(180/T)$	200–300	NASA, 1982[3]	(c)
$9.2\times 10^{-12}\exp(66/T)$	200–300	NASA, 1983[4]	(d)

Comments

(a) Discharge flow system. First-order decay of [OH] monitored by resonance fluorescence. Correction made for regeneration of OH by reaction $Cl + HO_2 \rightarrow HO + ClO$. Authors recommend temperature-independent value given above but also give expression: $k = (9.2 \pm 6.5) \times 10^{-12} \exp[(66 \pm 200)/T]$.

(b) Based on results of Leu and Lin.[5]

(c) Based on preliminary, uncorrected results of Ravishankara *et al.* and on results of Leu and Lin.[5]

(d) Based on results of Ravishankara *et al.*[1] and corrected results of Leu and Lin.[5]

Preferred Values

$k = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.2 \times 10^{-12} \exp(66/T)$ cm^3 molecule^{-1} s^{-1} over range 250–335 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are based on results reported by Ravishankara *et al.*[1] and the 298 K value of Leu and Lin.[5] The latter's published value, when corrected for regeneration of HO by reaction $Cl + HO_2 \rightarrow HO + ClO$, becomes 1.14×10^{-13} cm^3 molecule^{-1} s^{-1} (private communication). Leu and Lin also determined a lower limit of 0.65 for k_1/k at 298 K. The approach was somewhat indirect, and the actual value may be unity. If this ratio is unity, then the value of k and the value of k ($Cl + HO_2 \rightarrow HO + ClO$) are consistent with the value of 10.5 kJ mol^{-1} reported by Howard[6] for the heat of formation of HO_2.

References

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

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$ClO + O_2(^1\Delta) \rightarrow$ sym ClO_3

$\Delta H^\circ = -72.0$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leqslant 3 \times 10^{-15}$	298	Zellner and Handwerk, 1983[1]	(a)

Comments

(a) Flash photolysis–uv absorption technique. [ClO] decay monitored in presence of excess $O_2(^1\Delta)$ and in its absence. Observation that decay rate is not accelerated in presence of $O_2(^1\Delta)$ gives upper limit for k at pressure of 5 Torr.

Preferred Values

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

Comments on Preferred Values

Preferred value accepts the recent results of Zellner and Handwerk[1] in the only reported study of this reaction. This reaction is too slow to be of any significance in atmospheric chemistry.

References

[1] R. Zellner and V. Handwerk (unpublished, 1983).

$ClO + NO_2 + M \rightarrow ClONO_2 + M$

$\Delta H^\circ = -109$ 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			
$(1.5 \pm 0.2) \times 10^{-31}[N_2]$	298	Dasch, Sternberg, and Schindler, 1981[1]	(a)
$(1.8 \pm 0.4) \times 10^{-31}[N_2]$	270–295	Cox, Burrows, and Coker, 1984[2]	(b)
$(1.6 \pm 0.2) \times 10^{-31}(T/300)^{-3.0}[N_2]$	264–343	Handwerk and Zellner, 1984[3]	(c)
Reviews and Evaluations			
$1.6 \times 10^{-31}(T/300)^{-3.4}[N_2]$	250–420	CODATA, 1982[4]	(d)
$1.8 \times 10^{-31}(T/300)^{-3.4}[air]$	200–300	NASA, 1982[5]	(e)
$1.8 \times 10^{-31}(T/300)^{-3.4}[air]$	200–300	NASA, 1983[6]	(f)

Comments

(a) Laser flash photolysis generation of ClO radicals from Cl_2O. ClO radicals monitored by absorption at 285.2 nm using a Xe arc lamp or a Mg-hollow cathode lamp as light source. Pressure range 20–600 Torr. Results in good agreement with falloff curve from earlier studies.[4–6]

(b) Modulated photolysis of Cl_2–Cl_2O–NO_2–N_2 mixtures. $ClONO_2$ formation followed by diode laser spectroscopy. This study rules out the formation of isomers other than $ClONO_2$.

(c) Flash photolysis generation of ClO from Cl_2O. Detection of ClO via absorption at 256 nm. Pressure range 17–790 Torr, experiments at 264, 298, and 343 K. Results in good agreement with earlier data in the falloff range.[4–6]

(d) Average of several measurements which all agreed very well.

(e) As comment (d). In this evaluation the formation of two different isomers was assumed. The value given here is the sum of the two rate constants for these two isomers.

(f) As comment (d). The formation of a second isomer is now being ruled out.

Preferred Values

$k_0 = 1.7 \times 10^{-31}(T/300)^{-3.4}[N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

There is now excellent agreement between the various studies of the reaction in the falloff region near to the low-pressure limit. The preferred value is the average of ten different studies evaluated earlier[4] and in the present evaluation. The formation of OClONO or ClOONO, suggested in order to explain discrepancies between recombination and dissociation rate data, apparently does not occur (see experiments by Cox *et al.*, 1983[2] and Margitan, 1983[7]). The discrepancies now have to be attributed either to erroneous dissociation rate measurements or to uncertainties in the equilibrium constant. In the latter case, the factor of 3 discrepancy would require[6] a change in the ΔH° value of the reaction by about 4 kJ mol^{-1}.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3-6) \times 10^{-12}$	298	Dasch, Sternberg, and Schindler, 1983[1]	(a)
$(1.2^{+1.2}_{-0.6}) \times 10^{-11}$	264–343	Handwerk and Zellner, 1984[3]	(b)
Reviews and Evaluations			
2×10^{-11}	200–400	CODATA, 1982[4]	(c)
$3 \times 10^{-11}(T/300)^{-1.9}$	200–300	NASA, 1982[5]	(d)
$1.5 \times 10^{-11}(T/300)^{-1.9}$	200–300	NASA, 1983[6]	(e)

Comments

(a) See comment (a) of k_0. Extrapolation of k_∞ very uncertain. F_c unspecified.

(b) See comment (c) of k_0. Extrapolation of k_∞ very uncertain. Given k_∞ value based on theoretical prediction. Using the given k_0 and k_∞ values, and $F_c = 0.55, 0.50, 0.45$ for 264, 298, 343 K, respectively, falloff curves are obtained which are in good agreement with the majority of the available data.

(c) Based on a theoretical fit of experimental falloff curves.

(d) Sum of k_∞ values for the formation of two different isomers. Probably this number was assigned erroneously and one-half this value was meant.

(e) Assuming the formation of only one isomer. Corrects the value commented in (d). k_∞ and its temperature coefficient are based on theoretical modeling by Smith and Golden, *1979*.[8]

Preferred Values

$k_\infty = 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over range 200–300 K.

Comments on Preferred Values

Since there are no direct measurements of k_∞ at pressures above 1 atm, k_∞ cannot be established with certainty. Theoretical predictions are no better than within 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 in this range. For this reason, we suggest an unchanged preferred value with only a minor temperature dependence of k_∞.

Intermediate Falloff Range

As before we prefer $F_c = 0.5$ at 298 K. Representation in the form $F_c = \exp(-T/T^*)$ gives $T^* = 430$ K.

References

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HOCl + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$HOCl + h\nu \rightarrow HCl + O(^3P)$ (1)	230	520
$\rightarrow HO + Cl$ (2)	233	513
$\rightarrow ClO + H$ (3)	393	304
$\rightarrow HCl + O(^1D)$ (4)	420	285

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi_1 = 0.00 \pm 0.01$	308	Butler and Phillips, 1983[1]	(a)

Comments

(a) Laser photolysis. Production of O atoms looked for by resonance fluorescence at 130 nm. No evidence for O atom production was observed and an upper limit of approximately 0.02 (two standard deviations) can be placed on Φ_1.

Preferred Values

Absorption cross sections.

The preferred cross sections are unchanged from values tabulated in the previous CODATA evaluation.[2]

Quantum yields for HOCl photolysis.

$\Phi_2 = 1.0$ for $\lambda > 200$ nm.

Comments on Preferred Values

Absorption cross sections.

See previous CODATA evaluation.[2]

Quantum yields.

The preferred quantum yields are unchanged from the previous CODATA evauluation.[2] The upper limit for Φ_1 reported by Butler and Phillips[1] is consistent with the recommendation that photodissociation proceeds completely by (2) to give HO + HCl.

References

[1] P. J. D. Butler and L. F. Phillips, J. Phys. Chem. **87**, 183 (1983).

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

$ClONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH/kJ mol^{-1}	$\lambda_{threshold}$/nm
$ClONO_2 + h\nu \rightarrow ClO + NO_2$	(1)	109	1100
$\rightarrow Cl + NO_3$	(2)	166	721
$\rightarrow ClONO + O(^3P)$	(3)	306	391
$\rightarrow ClONO + O(^1D)$	(4)	496	241

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
Φ_3 is predominant $\Phi_2 < 0.04$	> 200	Adler-Golden and Wiesenfeld, 1981[1]	(a)
$\Phi_2 = 0.55(+0.3, -0.1)$	249	Marinelli and Johnston, 1982[2]	(b)
$\Phi_2 = 0.90 \pm 0.10$ $\Phi_3 \sim 0.10$ $\Phi_1 < 0.2$	266,355	Margitan, 1983[3]	(c)
$\Phi_2 = 0.90 \pm 0.05$ $\Phi_3 = 0.10 \pm 0.02$ $\Phi_4 < 0.05$	265,313	Knauth and Schindler, 1983[4]	(d)

Comments

(a) Flash photolysis at $\lambda > 200$ nm. O atoms observed by time-resolved resonance absorption at 131 nm. No resonance absorption by Cl atoms observed; upper limit for Φ_2 estimated to be about 4%. It was concluded that predominant photolysis channel is (3).

(b) Laser flash photolysis at 249 nm. $[NO_3]$ in its ground vibrational state monitored by time-resolved tunable dye-laser absorption at 662 nm and observed to be formed with an initial quantum yield of ~ 0.55.

(c) Laser photolysis at 266 and 355 nm. Cl atoms and O atoms observed by resonance fluorescence and signals compared with that from photolysis of reference molecule (Cl_2 or NOCl and NO_2). Observation that no additional Cl were produced upon addition of NO to photolysis mixture gives upper limit of 0.2 on Φ_1.

(d) Series of different experiments with product analysis by mass spectrometry or by ultraviolet or infrared absorption. Photolysis at 265 nm and 253 K in excess $^{15}NO_2$; $ClO^{15}NO_2$ production looked for, giving $\Phi_1 < 0.05$. O atom production at 265 nm determined by addition of up to 10% NO_2 and measurement of O_2 yield, giving $\Phi_3 = 0.10 \pm 0.02$. Low-temperature photolysis of $ClONO_2/NO_2$ mixtures; $\Phi(N_2O_5) = 0.90 \pm 0.05$ measured by infrared absorption. N_2O_5 results from scavenging of photoproduced NO_3 by NO_2, thus $\Phi(N_2O_5) = \Phi_2$. Quantum yield for O_2 production at 265 and 313 nm without any additive $\Phi(O_2) = 0.43 \pm 0.02$ independent of wavelength.

Preferred Values

Absorption cross sections.

The preferred cross sections are unchanged from values tabulated in the previous CODATA evaluation.[5]

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

Absorption cross sections.

See previous CODATA evaluation.[5]

Quantum yields.

The preferred quantum yield value of 0.9 for Φ_2 and a complementary value of 0.1 for Φ_3 are based on the direct results of Margitan.[3] They are confirmed by the results of Knauth and Schindler[4] based on final product analysis, and also by the earlier results of Chang *et al.*[7] The fact that Adler-Golden and Wiesenfeld[1] did not observe Cl atoms is understandable on the basis that they were scavenged by $ClONO_2$ before the time of observation with a rate coefficient now known to be much faster than previously thought (see data sheet on Cl + $ClONO_2$). The interpretation given for the results of Marinelli and Johnston[2] is erroneous because it too is based on the very low reported value for this rate coefficient.

References

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[2] W. J. Marinelli and H. S. Johnston, Chem. Phys. Lett. **93**, 127 (1982).

[3] J. J. Margitan, J. Phys. Chem. **87**, 674 (1983).

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4.8. Bromine Compounds

$O + HBr \rightarrow HO + Br$

$\Delta H^\circ = -61.9$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.7 \pm 1.9)\times 10^{-12} \exp[-(1537 \pm 81)/T]$	221–455	Nava, Bosco, and Stief, 1983[1]	(a)
$(3.37 \pm 0.35)\times 10^{-14}$	298		
Reviews and Evaluations			
$7.0\times 10^{-12} \exp(-1560/T)$	250–400	CODATA, 1982[2]	(b)
$7.6\times 10^{-12} \exp(-1570/T)$	200–300	NASA, 1982[3]	(c)
$6.6\times 10^{-12} \exp(\ 1540/T)$	200 300	NASA, 1983[4]	(d)

Comments

(a) Flash photolysis. First-order decay of [O] monitored by resonance fluorescence. Slight curvature in Arrhenius plot for $T < 298$ K noted.

(b) Based on fit to data for 250–400 K reported by Takacs and Glass,[5] Brown and Smith,[6] and Singleton and Cvetanovic.[7]

(c) Based on fit to same data as in (b) with preexponential factor fitted to value of k at 298 K.

(d) Based on fit to data of Nava *et al.*[1] and data of Singleton and Cvetanovic[7] over same temperature range.

Preferred Values

$k = 3.7\times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.6\times 10^{-12} \exp(-1540/T)$ cm^3 molecule^{-1} s^{-1} over range 220–455 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.

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

Comments on Preferred Values

The new study of Nava *et al.*[1] over the temperature range 221–455 K provides the only data measured at stratospheric temperatures. The preferred value is based on a fit to these data and the data of Singleton and Cvetanovic[7] over the same temperature range by a phase shift technique. These results are less subject to complications due to secondary chemistry than are the results of the discharge flow studies[5,6] at much lower ratios of $[HBr]_0$ to $[O]_0$.

References

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[2] CODATA Task Group on Chemical Kinetics, D. L. Baulch, R. A. Cox, P. J. Crutzen, R. F. Hampson, J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data **11**, 327 (1982).
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$O + Br_2 \rightarrow BrO + Br$

$\Delta H^\circ = -205.1$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.7 \pm 3.0)\times 10^{-12}$	300	Clyne and Cruse, 1971[1]	(a)
$(1.4 \pm 0.2)\times 10^{\ 11}$	298	Clyne, Monkhouse, and Townsend, 1976[2]	(b)
Relative Rate Coefficients			
1.4×10^{-11}	306–405	Moin, Yurkevitch, and Drogo'itskii, 1976[3]	(c)
Reviews and Evaluations			
1.39×10^{-11}	303	Baulch *et al.*[4]	(d)

Comments

(a) Discharge flow–resonance absorption detection of $O(^3P)$; excess NO present to convert BrO to Br and prevent removal of $O(^3P)$ by reaction with BrO product. $[Br_2]_0 \simeq [O]_0$, i.e., second-order kinetic conditions.

(b) Discharge flow–resonance fluorescence detection of $O(^3P)$ and $Br(^2P)$; decay of $O(^3P)$ in excess Br_2 and NO exhibited pseudo-first-order kinetics. k measured from $O(^3P)$ decay and also from $Br(^2P)$ production, the two methods giving the same result.

(c) Discharge flow; O monitored by EPR. Total pressure = 2.5 Torr. k measured relative to $k(O + Cl_2 \rightarrow ClO + Cl)$ by determination of the Cl_2 and Br_2 mass flows required to achieve the same reduction in [O]. Authors give $k/k(O + Cl_2) = 10^{0.6 \pm 0.53} \exp[-(1310 \pm 45)/T]$. Temperature-independent value given in Table is based on the analysis and preferred value for $k(O + Cl_2 \rightarrow ClO + Cl) = 4.7 \times 10^{-12} \exp(-1368/T)$ cm^3 $molecule^{-1}$ s^{-1} given by Baulch *et al.*,[4] using the authors' original data.

(d) Based on the results in Refs. 2 and 3.

Preferred Values

$k = 1.4 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$.

Comments on Preferred Values

The rate coefficient is reasonably well defined by the results of Clyne, Monkhouse, and Townsend[2] and Moin *et al.*[3] The earlier data[1] was reinterpreted[2] giving a revised value of $(1.2 \pm 0.4) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. The preferred value is based on the results from Refs. 2 and 3. Since no measurements at temperatures below 298 K have been reported we do not give a preferred value for the temperature range of interest for the atmosphere. The results of Moin *et al.*[3] suggest near-zero temperature dependence, as expected for a fast reaction of this type.

References

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[2] M. A. A. Clyne, P. B. Monkhouse, and L. W. Townsend, Int. J. Chem. Kinet. **8**, 425 (1976).
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Br + HCHO→HBr→HCO

$\Delta H° = -2.1$ kJ mol^{-1}

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.97 \pm 0.60) \times 10^{-11} \exp[-(1015 \pm 70)/T]$	295–480	Poulet, Laverdet, and Le Bras, 1981[1]	(a)
$(9.4 \pm 0.8) \times 10^{-13}$	295		
Reviews and Evaluations			
$1.4 \times 10^{-11} \exp(-750/T)$	223–480	CODATA, 1982[2]	(b)
$1.7 \times 10^{-11} \exp(-800/T)$	200–300	NASA, 1983[3]	(c)

Comments

(a) Discharge flow–mass spectrometic detection of HCHO in excess Br; earlier data of LeBras *et al.*[4] shown to be in error due to secondary reaction of Br with HCO.

(b) Based on data from the flash photolysis–resonance fluorescence study of Nava *et al.*[5]

(c) Arrhenius expression obtained by least-squares fit of data from Poulet *et al.*[1] and Nava *et al.*[5]

Preferred Values

$k = 1.0 \times 10^{-12}$ 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 range 223–480 K.

Reliability

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

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

Comments on Preferred Values

The new data[1] are in good agreement with the earlier work[5] for the temperature range 295–480 K. The Arrhenius expression recommended by NASA,[3] obtained by least-squares fit to the data from Refs. 1 and 5 is therefore accepted for this evaluation. The earlier data[5] covered a wider temperature range 223–480 K and gave a lower activation energy than the new data.[5] The authors[5] suggest that curvature in the Arrhenius plot is not unexpected for this reaction on theoretical grounds and expressions of the type $AT^{-1/2} \exp(-E/RT)$ were shown to "fit" the data well. The preferred value for k at 298 K is a simple mean of the values at 295 and 298 K from Refs. 1 and 5.

References

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$HO + HBr \rightarrow H_2O + Br$

$\Delta H^\circ = -132.6$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.2 \pm 0.7) \times 10^{-12}$	298	Jourdain, LeBras, and Combourieu, 1981[1]	(a)
$(6.0 \pm 0.32) \times 10^{-12}$	298	Husain, Plane, and Slater, 1981[2]	(b)
Reviews and Evaluations			
8.5×10^{-12}	249–416	CODATA, 1982[3]	(c)
8.0×10^{-12}	200–300	NASA, 1982[4]	(d)
8.0×10^{-12}	200–300	NASA, 1983[5]	(d)

Comments

(a) Discharge flow–EPR technique.

(b) Flash photolysis–resonance fluorescence technique.

(c) Based on results of Takacs and Glass[6] and Ravishankara *et al.*[7]

(d) Based on results of Takacs and Glass,[6] Ravishankara *et al.*,[7] Jourdain *et al.*,[1] and Husain *et al.*[2]

Preferred Values

$k = 8.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 249–416 K.

Reliability

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

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

Comments on Preferred Values

There have been two measurements of this rate by the discharge flow–EPR technique; Takacs and Glass[6] and Jourdain *et al.*[1] report values of 5.1 and 9.2×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively. There have also been two measurements by the flash photolysis–resonance fluorescence technique; Ravishankara *et al.*[7] and Husain *et al.*[2] report values of 11.9 and 6.0×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively. The preferred value of k at 298 K is the mean of these values. The temperature independence over the range 249–416 K is based on the results of Ravishankara *et al.*[7]

References

[1] J. L. Jourdain, G. LeBras, and J. Combourieu, Chem. Phys. Lett. **78**, 483 (1981).

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[4] NASA Panel for Data Evaluation, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 5*, W. B. DeMore, R. T. Watson, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, M. J. Molina, and A. R. Ravishankara, JPL Publ. 82-57 (1982).

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[7] A. R. Ravishankara, P. H. Wine, and A. O. Langford, Chem. Phys. Lett. **63**, 479 (1979).

$HO + Br_2 \rightarrow HOBr + Br$

$\Delta H^\circ = -38$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.2 \pm 0.7) \times 10^{-11}$	298	Poulet, Laverdet, and LeBras, 1983[1]	(a)

J. Crutzen, R. F. Hampson, J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data **11**, 327 (1982).

[3] NASA Panel for Data Evaluation, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, W. B. DeMore, R. T. Watson, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, M. J. Molina, and A. R. Ravishankara, JPL Publ. 82-57 (1982).

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[5] D. F. Nava, J. V. Michael, and L. J. Stief, J. Phys. Chem. **85**, 1896 (1981).

$HO + HBr \rightarrow H_2O + Br$

$\Delta H^\circ = -132.6$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.2 \pm 0.7) \times 10^{-12}$	298	Jourdain, LeBras, and Combourieu, 1981[1]	(a)
$(6.0 \pm 0.32) \times 10^{-12}$	298	Husain, Plane, and Slater, 1981[2]	(b)
Reviews and Evaluations			
8.5×10^{-12}	249–416	CODATA, 1982[3]	(c)
8.0×10^{-12}	200–300	NASA, 1982[4]	(d)
8.0×10^{-12}	200–300	NASA, 1983[5]	(d)

Comments

(a) Discharge flow–EPR technique.

(b) Flash photolysis–resonance fluorescence technique.

(c) Based on results of Takacs and Glass[6] and Ravishankara *et al.*[7]

(d) Based on results of Takacs and Glass,[6] Ravishankara *et al.*,[7] Jourdain *et al.*,[1] and Husain *et al.*[2]

Preferred Values

$k = 8.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 249–416 K.

Reliability

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

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

Comments on Preferred Values

There have been two measurements of this rate by the discharge flow–EPR technique; Takacs and Glass[6] and Jourdain *et al.*[1] report values of 5.1 and 9.2×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively. There have also been two measurements by the flash photolysis–resonance fluorescence technique; Ravishankara *et al.*[7] and Husain *et al.*[2] report values of 11.9 and 6.0×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively. The preferred value of k at 298 K is the mean of these values. The temperature independence over the range 249–416 K is based on the results of Ravishankara *et al.*[7]

References

[1] J. L. Jourdain, G. LeBras, and J. Combourieu, Chem. Phys. Lett. **78**, 483 (1981).

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[7] A. R. Ravishankara, P. H. Wine, and A. O. Langford, Chem. Phys. Lett. **63**, 479 (1979).

$HO + Br_2 \rightarrow HOBr + Br$

$\Delta H^\circ = -38$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.2 \pm 0.7) \times 10^{-11}$	298	Poulet, Laverdet, and LeBras, 1983[1]	(a)

Comments

(a) Discharge flow–HO measured by both EPR and laser induced fluorescence, giving identical results. Measurement of Br formed using EPR showed that reaction proceeds exclusively by the above channel.

Preferred Value

$k = 4.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

This is the only reported kinetic measurement of the HO + Br_2 reaction. The rate constant is consistent with the similarly rapid reactions of O and H with Br_2, and is expected to have zero or very small temperature dependence.

References

[1] G. Poulet, G. Laverdet, and G. LeBras, Chem. Phys. Lett. **94**, 129 (1983).

$BrO + HO_2 \rightarrow HOBr + O_2$ (1)
$\rightarrow HBr + O_3$ (2)

$\Delta H^\circ(1) = -215$ kJ mol^{-1}
$\Delta H^\circ(2) = -29$ 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			
$(5^{+5}_{-3}) \times 10^{-12}$	303	Cox and Sheppard, 1982[1]	(a)
Reviews and Evaluations			
5×10^{-12}	298	CODATA, 1982[2]	(b)
5×10^{-12}	298	NASA, 1982[3]	(c)
5×10^{-12}	298	NASA, 1983[4]	(c)

Comments

(a) Molecular modulation–uv absorption detection of BrO and HO_2. Photolysis of O_3 in presence of Br_2, H_2, and O_2 to produce BrO and HO_2. Rate coefficient obtained from computer fits to data using a complex mechanism. The analysis gave values in the range $(2.3\text{–}6.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} with a best estimate and error limits given above.

(b) Estimate based on analogous reaction of ClO.

(c) Based on data of Cox and Sheppard[1] and the analogy with ClO + HO_2 reaction.

Preferred Value

$k = 5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Value

The new results[1] demonstrate that a moderately rapid reaction occurs between HO_2 and BrO at room temperature, according to either or both of the above channels. The quality of the rate data is not sufficient to justify any change in the preferred value or its reliability, from the previous evaluations.

References

[1] R. A. Cox and D. W. Sheppard, J. Chem. Soc. Faraday Trans. 2 **78**, 1383 (1982).
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[4] NASA Panel for Data Evaluation, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 6*, W. B. DeMore, M. J. Molina, R. T. Watson, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, and A. R. Ravishankara, JPL Publ. 83-62 (1983).

$BrO + BrO \rightarrow 2Br + O_2$ (1)
$\rightarrow Br_2 + O_2$ (2)

$\Delta H^\circ(1) = -28$ kJ mol^{-1}
$\Delta H^\circ(2) = -256$ 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			
$k_2 = (6.6 \pm 1.5)\times 10^{-13}$	278–338	Cox, Sheppard, and Stevens, 1982[1]	(a)
Branching Ratios			
$k_1/k_2 = 14.6 \exp[-(276 \pm 35)/T]$	258–333	Jaffe and Mainquist, 1980[2]	(b)
$k_1/k = 0.84 \pm 0.03$	298		
$k_1/k_2 = 130 \exp[-(992 \pm 210)/T]$	278–348	Cox, Sheppard, and Stevens, 1982[1]	(b)
$k_1/k = 0.84 \pm 0.03$	298		
Reviews and Evaluations			
2.8×10^{-12}	200–400	CODATA, 1982[3]	(c)
$k_1 = 1.4\times 10^{-12} \exp(+150/T)$ $k_2 = 6.0\times 10^{-14} \exp(+600/T)$	200–300	NASA, 1982[4]	(d)
$k_1 = 1.4\times 10^{-12} \exp(+150/T)$ $k_2 = 6.0\times 10^{-14} \exp(+600/T)$	200–300	NASA, 1983[5]	(d)

Comments

(a) Molecular modulation–uv absorption detection of BrO in the photolysis of Br_2–O_3–N_2 mixtures. Absorption cross section of BrO at $\lambda = 338.3$ nm determined in the same study. $\sigma = (1.7 \pm 0.3)\times 10^{-17}$ cm^3 molecule^{-1}, $10^{-4}k/\sigma(\text{cm s}^{-1}) = 4.2, 3.75, 3.50, 3.74$, at 277.5, 303, 325, and 348 K, respectively.

(b) Quantum yield for Br_2 photosensitized decomposition of O_3 determined. Ratio k_1/k_2 determined assuming a simple chain mechanism involving competition between propagation reaction (1) and termination reaction (2), to explain the temperature-dependent quantum yields.

(c) Based on direct measurements of Clyne and Watson[6] and Sander and Watson.[7]

(d) The value of k_1 is obtained from k ($= k_1 + k_2$) based on the data of Clyne and Watson[6] and Sander and Watson[6] and $k_1/k = 1.18 \exp(-104/T)$, a mean value, from the results of Cox *et al.*[1] and Jaffe and Mainquist.[2] k_2 expressions obtained from values of k_2 at 200 and 300 K obtained by difference. The uncertainties on E/R cover possible temperature-independent rate coefficients for either or both channels.

Preferred Values

$k_1 = 2.2\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 4.5\times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.1\times 10^{-12} \exp(+255/T)$ cm^3 molecule^{-1} s^{-1} over range 223–398 K.

Reliability

$\Delta \log k_1 = \pm 0.1$ at 298 K.
$\Delta \log k_2 = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The data base for this reaction is still rather unsatisfactory. The new value of k_2 is almost a factor of 2 higher than the only previous determination for this channel by Sander and Watson,[7] i.e., $k = 3.8\times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The ratio $k_1/k = 0.84 \pm 0.03$ at 298 K obtained in Ref. 7 agrees well with the corresponding values obtained from the quantum yield studies.[1,2] However, this could be fortuitous since the simple mechanism used[1,2] to evaluate the ratio did not give a full explanation of the quantum yield data. Also the temperature dependence of the quantum yields in the two studies was not in good agreement and utilization of the ratios to obtain temperature-dependent rate coefficients for the two reaction channels is subject to considerable uncertainty.

The preferred expression for the temperature dependence of the overall rate coefficient is that from the NASA evaluation 5 and is based on the results of Ref. 7, with the A factor adjusted to give a value of k at 298 K equal to the mean of the experimental values from Refs. 6 and 7 at this temperature. The uncertainty in (E/R) is reduced from our previous evaluation[3] since the positive temperature dependence reported by Clyne and Cruse[8] can probably be attributed to the temperature dependence of the absorption cross section σ, found by Sander and Watson.[7] The preferred values for the two channels at 298 K are based on the preferred value of k at 298 K and the ratio $k_1/k = 0.84$. In view of the uncertainties noted above, no recommendation is given for the temperature dependence of the individual channels.

References

[1] R. A. Cox and D. W. Sheppard, J. Photochem. **19**, 189 (1982).
[2] S. Jaffe and W. K. Mainquist, J. Phys. Chem. **84**, 3277 (1980).
[3] CODATA Task Group on Chemical Kinetics, D. L. Baulch, R. A. Cox, P. J. Crutzen, R. F. Hampson, J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data **11**, 327 (1982).
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[7]S. P. Sander and R. T. Watson, J. Phys. Chem. **85**, 4000 (1981).
[8]M. A. A. Clyne and H. W. Cruse, Trans. Faraday Soc. **66**, 2214 (1970).

$BrO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ mol^{-1}	$\lambda_{threshold}$/nm
$BrO + h\nu \rightarrow Br + O(^3P)$ (1)	232	515
$\rightarrow Br + O(^1D)$ (2)	422	283

Absorption cross-section data

Wavelength/nm	Reference	Comment
296–375	Cox, Sheppard, and Stevens, 1982[1]	(a)

Comments

(a) Molecular modulation study of photolysis of Br_2–O_3 mixtures. Absorption measurements at 0.1 nm intervals and 0.22 nm resolution. Absolute absorption cross sections based on determination of the cross section for the most intense band in the $A\,^2\Pi$–$X\,^2\Pi$ vibrational progression at 338.3 nm, $(v' = 7) \leftarrow (v'' = 0)$,[2] from measurements of BrO kinetics. The value obtained for σ(7-0) was $(1.8 \pm 0.3) \times 10^{-17}$ cm^2 molecule^{-1} over the temperature range 277–348 K. Average values over 5 nm intervals are given.

Preferred Values

Absorption cross sections

λ/nm	$10^{18}\ \sigma$/cm^2	λ/nm	$10^{18}\ \sigma$/cm^2
300–305	2.00	340–345	5.15
305–310	2.59	345–350	3.99
310–315	4.54	350–355	2.28
315–320	3.91	355–360	1.72
320–325	6.00	360–365	1.61
325–330	7.53	365–370	0.92
330–335	6.28	370–375	0.51
335–340	5.89		

Comments on Preferred Values

The preferred values are those tabulated in Ref. 1. Comparison of cross-section data from different sources is difficult because of the diverse spectral bandwidths used. However the new data[1] for the cross section in the 7-0 band at 339 nm [$\sigma = (9.0 \pm 1.5) \times 10^{-18}$ cm^2 molecule^{-1}], agree with the measurement of Sander and Watson[3] [σ,(339.0 nm) = 1.17×10^{-17} cm^2 molecule^{-1} at 298 K]. The latter remains the most reliable determination at a single wavelength since it does not depend on kinetic parameters. The earlier determinations of σ,[4,5] which gave lower values, are less reliable[3,6] and are neglected. The estimated uncertainty on σ is $+20\%$–50%. Sander and Watson[3] also report a temperature dependence of σ at 339 nm in the 7-0 band over the range 220–388 K but this is unlikely to affect the 5 nm averaged values of σ.

References

[1]R. A. Cox, D. W. Sheppard, and M. P. Stevens J. Photochem. **19**, 189 (1982).
[2]M. Barnett, E. A. Cohen, and D. A. Ramsay, Can. J. Phys. **59**, 1908 (1982).
[3]S. P. Sander and R. T. Watson, J. Phys. Chem. **85**, 4000 (1981).
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[5]N. Basco and S. K. Dogra, Proc. R. Soc. London Ser. A **323**, 1 (1971).
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4.9. Iodine Compounds

$O + I_2 \rightarrow IO + I$

$\Delta H^\circ = -32.8$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.38 \pm 0.44) \times 10^{-10}$	298	Ray and Watson, 1982[1]	(a)

Comments

(a) Discharge flow–mass spectrometric detection of I_2 in the presence of large excess O atoms. [O] determined by titration with NO_2. Total pressure 2.0 Torr.

Preferred Values

$k = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over 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 value of k is consistent with the trend observed in the rate coefficients for the $O + X_2$ reaction, which increase steadily: $\leqslant 1 \times 10^{-15}$ 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 (CODATA Evaluation) at 298 K. The molecular beam study of Parrish and Herschbach,[4] suggests zero activation energy which is consistent with the near gas kinetic value of k at 298 K.

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] D. D. Parrish and D. R. Herschbach, J. Am. Chem. Soc. **95**, 6133 (1973).

$IO + NO_2 + M \rightarrow IONO_2 + M$

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.3 \pm 2.0) \times 10^{-31}[N_2]$	277	Jenkin and Cox, 1984[1]	(a)
Reviews and Evaluations			
$5.0 \times 10^{-31}(T/300)^{-3}[N_2]$	200–400	CODATA, 1982[2]	(b)

Comments

(a) Molecular modulation; IO monitored in absorption at 427 nm in excess NO_2. I_2 photolysis in presence of O_3 to produce IO. Pressure range 35–404 Torr N_2. Falloff curve analyzed by method of Troe[3] using a value of $F_c = 0.4$ derived by analogy with the $BrO + NO_2$ reaction. Small correction for second-order component in IO kinetics at higher pressures.

(b) Based on analogy with $BrO + NO_2 + M$ reaction.

Preferred Values

$k_0 = 3.4 \times 10^{-31}[N_2]$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_0 = 3.4 \times 10^{-31}(T/300)^{-3}[N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred value at 298 K is based on the measurements of Jenkin and Cox[1] at 277 K and an assumed T dependence of $(T/300)^{-3}$ based on analogy to the $ClO + NO_2$ reaction. The single experimental study requires independent confirmation.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.6^{+0.6}_{-0.8}) \times 10^{-11}$	277	Jenkin and Cox, 1984[1]	(a)

Comments

(a) See comment (a) for k_0. Value obtained from a fit to the falloff curve using $F_c = 0.4$.

Preferred Value

$k_\infty = 1.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over range 200–400 K.

Comments on Preferred Value

This is a reasonable value for reactions of this type; however an independent confirmation is required.

Intermediate Falloff Range

From the preferred values one calculates $[N_2]_c = 5.0\times10^{19}$ molecule cm^{-3} at 298 K. The value of $F_c = 0.4$ was taken to be the same as for the $BrO + NO_2$ reaction as derived using the theoretical techniques of Troe[3] by Sander *et al.*[4]

References

[1] M. E. Jenkin and A. R. Cox, J. Phys. Chem. (in press).
[2] CODATA Task Group on Chemical Kinetics, D. L. Baulch, R. A. Cox, P. J. Crutzen, R. F. Hampson, J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data **11**, 327 (1982).
[3] J. Troe, J. Phys. Chem. **83**, 114 (1979).
[4] S. P. Sander, G. W. Ray, and R. T. Watson, J. Phys. Chem. **85**, 199 (1981).

$IO + IO \rightarrow 2I + O_2$ (1)
$\rightarrow I_2 + O_2$ (2)
$IO + IO + M \rightarrow I_2O_2 + M$ (3)

$\Delta H^\circ(1) = -130$ kJ mol^{-1}
$\Delta H^\circ(2) = -282$ 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			
$(4.0^{+2.8}_{-2.0})\times10^{-10}$	303	Cox and Coker, 1983[1]	(a)
Reviews and Evaluations			
3×10^{-12}	298	CODATA, 1982[2]	(b)

Comments

(a) Molecular modulation; IO produced by $I + O_3$ reaction and detected in absorption at 426.9 nm. Total pressure = 1 atm; overall reaction of IO led to aerosol products. A value of $k/\sigma(426.9\ \text{nm}) = (1.3\pm0.3)\times10^7$ cm s^{-1} reported. The value of k given is based on $\sigma = (3.1^{+2.1}_{-1.5})\times10^{-17}$ cm^2 determined in the same study, and is defined using the equation $-d[IO]/dt = k[IO]^2$.

(b) Based on discharge flow results of Clyne and Cruse.[3]

Preferred Values

No recommendation.

Comments on Preferred Values

Both experimental studies of this reaction used absorption spectroscopy to monitor IO and therefore a knowledge of σ is required.

The previous CODATA recommendation[2] for k is almost certainly too low since it is based on a value of $\sigma = 5\times10^{-18}$ cm^2 estimated by Clyne and Cruse.[3] The new value[1] of σ would lead to a value of $k = 2.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} based on the work of Clyne and Cruse,[3] where k is defined by $-d[IO]/dt = k[IO]^2$. The new data gives a value of k/σ considerably higher than that obtained in the earlier study,[3] $k/\sigma = 1.0\times10^6$ cm s^{-1}. This may suggest a change of mechanism over the pressure range 1–760 Torr or that one or both the measurements are incorrect.

Neither study provides positive evidence for channel (1), which is expected to be an important pathway by analogy with other $XO + XO$ reactions ($X = F$, Cl, Br). In view of the apparent complexity of the $IO + IO$ reaction we are unable to make a recommendation for k or the branching ratio at this time.

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$IO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$IO + h\nu \rightarrow I + O(^3P)$ (1)	184	651
$\rightarrow I + O(^1D)$ (2)	374	320

Absorption cross-section data

Wavelength/nm	Reference	Comment
415–470	Cox and Coker, 1983[1]	(a)

Comments

(a) Molecular modulation study using photolysis of I_2 or CH_3I in the presence of O_3. Absorption due to $A^2\Pi \leftarrow X^2\Pi$ transition in the indicated wavelength range recorded at 0.25 nm intervals with spectral resolution of 0.27 nm. Absolute cross sections based on kinetic measurements of IO monitored at the band head of the $(v' = 4) \leftarrow (v'' = 0)$ band at 426.9 nm for which $\sigma = (3.1^{+2.0}_{-1.5}) \times 10^{-17}$ cm^2. σ values averaged over 5 nm intervals also given.

Preferred Values

Absorption cross sections

λ/nm	$10^{18}\ \sigma$/cm^2	λ/nm	$10^{18}\ \sigma$/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		

Comments on Preferred Values

The preferred absorption cross sections are taken from the table given by Cox and Coker.[1] The uncertainty is due mainly to that associated with the measurement of σ(426.9 nm) which is estimated to be ± a factor of 3.

No recommendation is given for the quantum yield. Durie and Ramsay[2] report extensive predissociation in the $A \leftarrow X$ progression of IO, therefore the quantum yield for process (1) is probably unity throughout the wavelength region of the preferred σ values.

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Appendix I

Enthalpy Data

(Substance)	$\Delta H_f^\circ(298)$ kJ mol^{-1}	$\Delta H_f^\circ(0)$ kJ mol^{-1}	Notes
H	217.997	216.03	1
H_2	0	0	1
O	249.17	246.78	1
$O(^1D)$	438.9	436.6	2
O_2	0	0	1
$O_2(^1\Delta)$	94.3	94.3	2
$O_2(^1\Sigma)$	156.9	156.9	2
O_3	142.7	145.4	3
HO	39.0	38.7	3
HO_2	10.5 ± 4.2		30
H_2O	− 241.81	− 238.92	1
H_2O_2	− 136.32	− 130.04	3
N	472.68	470.82	1
N_2	0	0	1
NH	343	343	2
NH_2	185	188	7
NH_3	− 45.94	− 38.95	1
NO	90.25	89.75	3
NO_2	33.2	36.0	3
NO_3	71 ± 20	77 ± 20	4
N_2O	82.05	85.50	3
N_2O_4	9.1	18.7	4
N_2O_5	11.3	23.8	3
HNO	99.6	102.5	4
HNO_2	− 79.5	− 74	3
HNO_3	− 135.06	− 125.27	3
HO_2NO_2	− 54 ± 20		8
CH	594.1	590.8	4
CH_2	386	386	6
CH_3	145.6	149.0	4
CH_4	− 74.81	− 66.82	3
CN	435		4
HCN	135		4
NCO	159		5
CO	− 110.53	− 113.81	1
CO_2	− 393.51	− 393.14	1
HCO	37.6	37.2	9
CH_2O	− 108.6	− 104.7	2
HCOOH	− 378.6	− 371.6	3
CH_3O	14.6	22.6	9
CH_3O_2	16 ± 8		10
CH_2OH	− 25.9		20
CH_3OH	− 200.7	− 189.7	3
CH_3OOH	− 131		9
CH_3ONO	− 65.3	− 52.6	9
CH_3ONO_2	− 119.7	− 103.4	9
C_2H	536		20
C_2H_2	227.36		27
C_2H_3	285		20
C_2H_4	52.09		27
C_2H_5	107.5		2
C_2H_6	− 83.8	− 68.3	2
CH_2CN	245		20
CH_3CN	80		9
CH_2CO	− 59.54		27
CH_3CO	− 24.3		20
CH_3CHO	− 166.2		27
C_2H_5O	− 17.2		20
CH_2CH_2OH	− 55.2		31
C_2H_5OH	− 235.30 ± 0.29		27
CH_3CO_2	− 207.5		20
$C_2H_5O_2$	− 7.5		9
CH_3OOCH_3	− 125.5		9
C_3H_5	164.9		20
C_3H_6	20.2		27
n-C_3H_7	94.6 ± 7.5		20

Enthalpy data—Continued

(Substance)	$\Delta H_f^\circ(298)$ kJ mol^{-1}	$\Delta H_f^\circ(0)$ kJ mol^{-1}	Notes
i-C_3H_7	76.2 ± 6.3		20
C_3H_8	− 103.89 ± 0.59		27
C_2H_5CHO	− 187.4		27
CH_3COCH_3	− 217.2		27
CH_3CHCH_2OH	− 75.3		32
S	276.98	274.72	1
S_2	128.49	128.20	1
HS	146 ± 4	145 ± 4	11
H_2S	− 20.63	− 17.70	3
SO	5.0	5.0	5
SO_2	− 296.81	− 294.26	1
SO_3	− 395.7	− 390	3
SOH	21 ± 17		11
HSO_3	− 481 ± 25		12
CS	272	268	11
CS_2	117.2	116.6	3
CH_3SCH_3	− 37.2		11
CH_3SSCH_3	− 24.3		11
OCS	− 142	− 142	3
F	79.39	77.28	1
F_2	0	0	1
HF	− 273.30	− 273.26	1
HOF	− 98 ± 4	− 95 ± 4	6
FO	109 ± 8	109 ± 8	9
FO_2	50 ± 12	52 ± 12	9
$FONO$	− 63.4		13
FNO_2	− 25.4		13
$FONO_2$	10	18	4
CF_2	− 182 ± 8	− 182 ± 8	4
CF_3	− 470 ± 4	− 468 ± 4	4
CF_4	− 933	− 927	18
FCO	− 170 ± 60	− 170 ± 60	4
COF_2	− 634.7	− 631.6	3
Cl	121.30	119.62	1
Cl_2	0	0	1
HCl	− 92.31	− 92.13	1
ClO	102	102	2,14
$ClOO$	89 ± 5	91	2,14
$OClO$	97 ± 8	100 ± 8	14,15
ClO_3	155		3
Cl_2O	81.4	83.2	15
$HOCl$	− 78	− 75	2,16
$ClNO$	51.7	53.6	6
$ClNO_2$	12.5	18.0	3
$ClONO$	83		17
$ClONO_2$	26.4		15
FCl	− 50.7	− 50.8	4
CCl	502 ± 20	498 ± 20	4
CCl_2	238 ± 20	237 ± 20	4
CCl_3	79.5	80.1	4
CCl_4	− 95.8	− 93.6	18
$CHCl_3$	− 102.9	− 98.0	18
CH_2Cl	125		19
CH_2Cl_2	− 95.4	− 88.5	18
CH_3Cl	− 82.0	− 74.0	18
$ClCO$	− 17		9
$COCl_2$	− 220.1	− 218.4	2
$CFCl$	30 ± 25	30 ± 25	24
$CFCl_2$	− 96		20
$CFCl_3$	− 284.9	− 281.8	21
CF_2Cl	− 269		20
CF_2Cl_2	− 493.3	− 489.1	21
CF_3Cl	− 707.9	− 702.9	21
$CHFCl_2$	− 284.9	− 279.5	21
CHF_2Cl	− 483.7	− 477.4	21
$COFCl$	− 427 ± 33	− 423 ± 33	4
C_2Cl_4	− 12.4	− 11.9	4
C_2HCl_3	− 7.8	− 4.3	3
CH_2CCl_3	45 ± 30		25

Enthalpy data—Continued

(Substance)	$\Delta H_f^\circ(298)$ kJ mol^{-1}	$\Delta H_f^\circ(0)$ kJ mol^{-1}	Notes
CH_3CCl_3	– 142.3	– 145.0	22
Br	111.86	117.90	1
Br_2	30.91	45.69	1
HBr	– 36.38	– 28.54	1
HOBr	– 80 ± 8		9
BrO	125	133	3
BrNO	82.2	91.5	3
$BrONO_2$	20 ± 30		26
BrCl	14.6	22.1	4
CH_2Br	163		19
CH_3Br	– 37.7	– 22.3	23
I	106.762		1
$I_2(g)$	62.421		1
HI	26.36		1
IO	172		28
INO	121.3	124.3	29
INO_2	60.2	66.5	29

Notes

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