Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, Organic Species: Supplement VII

IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry

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This paper updates and extends part of the previous data base of critical evaluations of the kinetics and photochemistry of gas-phase chemical reactions of neutral species involved in atmospheric chemistry [J. Phys. Chem. Ref. Data **9**, 295 (1980); **11**, 327 (1982); **13**, 1259 (1984); **18**, 881 (1989); **21**, 1125 (1992); **26**, 521 (1997); **26**, 1329 (1997)]. The present evaluation is limited to the organic family of atmospherically important reactions. The work has been carried out by the authors under the auspices of the IUPAC Subcommittee on Gas Phase Kinetic Data Evaluation for Atmospheric Chemistry. Data sheets have been prepared for 171 thermal and photochemical reactions, containing summaries of the available experimental data with notes giving details of the experimental procedures. For each thermal 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. For each photochemical reaction the data sheets list the preferred values of the photoabsorption cross sections and the quantum yields of the photochemical reactions together with comments on how they were selected. 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 values of enthalpies of formation of the reactant and product species. © *1999 American Institute of Physics and American Chemical Society.* [S0047-2689(99)00102-6]

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

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Contents

1. Preface

This paper is Supplement VII 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 Supplement I in 1982[2] and Supplement II in 1984.[3] The original evaluation and Supplements I and II were primarily intended to furnish a kinetic data base for modeling middle atmosphere chemistry (10–55 km altitude).

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

This subcommittee produced Supplement III in 1989,[4] Supplement IV in 1992,[5] and Supplements V and VI in 1997,[6,7] in which the original data base was extended and updated to include more reactions involved in tropospheric chemistry. Since it was not possible to cope with all of the very large number of chemical reactions involved in tropospheric chemistry, it was originally decided to limit the coverage to those organic reactions for which kinetic or photochemical data exist for species containing up to three carbon atoms.

With the publication of Supplement V in 1997,[6] the data base had become so extensive that the Subcommittee decided that future supplements would be limited to dealing in turn with parts of the set of over 700 gas-phase and heterogeneous reactions. To this end Supplement VI was an update and extension of the following families of gas-phase reactions: O_x, HO_x, NO_x, and SO_x. Supplement VII continues this policy by updating and extending the reactions of organic species, last reviewed in Supplement V. In addition, the data base of atmospherically important organic reactions is widened in Supplement VII by the inclusion of C_4 organic reactions resulting from the atmospheric oxidation of butane. Future supplements will deal with: (i) heterogeneous reactions and (ii) halogen reactions. Since the present and future supplements will be much smaller than Supplement V, they will be published on a shorter time scale than those between Supplements I and V.

Following the pattern of Supplements V[6] and VI,[7] here we provide a data sheet for each of the reactions considered. Each data sheet provides as before a preferred rate coefficient, together with a statement of the assigned uncertainty limits, a comment giving the basis for the recommendation, and a list of the relevant references. Supplement VII also lists the data used in the selection of the Preferred Values for each reaction. This means that in Supplement VII some of the earlier data, omitted during the development of Supplements I–V, have been re-entered on the data sheets. This change, initiated with Supplement VI, is intended to aid the reader in appreciating how the Preferred Values were selected. To the extent that this information suffices, the reader can use the present publication without need to refer to the previous publications in the series. However, it should be emphasized that in preparing the updated data sheets, we have not listed all of the previous data contained in the original evaluation[1] and Supplements I–V.[2–6] Consequently for many reactions, to obtain the complete data set and historical background to the preferred rate parameters, it is recommended that the present supplement be read in conjunction with its predecessors.[1–6]

The cutoff point for literature searching for this supplement was the end of 1997. As in our previous evaluations, we also include data which were available to us in preprint form at that point.

2. Sumary of Reactions and Preferred Rate Data

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

Page No.	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$^{a}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
	Organic Reactions					
204	$O+CH_3 \rightarrow$ products	1.2×10^{-10}	±0.1	1.2×10^{-10}	290–900	±100
206	$O(^1D)+CH_4 \rightarrow HO+CH_3$ $\rightarrow CH_3O$ or CH_2OH+H $\rightarrow HCHO+H_2$	1.5×10^{-10}	±0.1	1.5×10^{-10}	200–350	±100
207	$HO+CH_4 \rightarrow H_2O+CH_3$	6.4×10^{-15}	±0.08	$2.15\times10^{-12}\exp(-1735/T)$	240–300	±100
209	$HO+C_2H_2+M \rightarrow C_2H_2OH+M$	5.0×10^{-30} [N_2] (k_0)	±0.1	$5\times10^{-30}(T/300)^{-1.5}$ [N_2]	300–800	$\Delta n=\pm1.5$
		No recommendation (see data sheet) (k_∞)				
211	$HO+C_2H_4+M \rightarrow C_2H_4OH+M$	7×10^{-29} [N_2] (k_0)	±0.3	$7\times10^{-29}(T/300)^{-3.1}$ [N_2]	200–300	$\Delta n=\pm2$
		9×10^{-12} (k_∞)	±0.3	9×10^{-12}	200–300	$\Delta n=\pm0.5$
		$F_c=0.48$				
214	$HO+C_2H_6 \rightarrow H_2O+C_2H_5$	2.5×10^{-13}	±0.08	$7.8\times10^{-12}\exp(-1025/T)$	240–300	±100
215	$HO+C_3H_6+M \rightarrow C_3H_6OH+M$	8×10^{-27} [N_2] (k_0)	±1.0	$8\times10^{-27}(T/300)^{-3.5}$ [N_2]	200–300	$\Delta n=+1$
		3.0×10^{-11} (k_∞)	±0.1	3.0×10^{-11}	200–300	$\Delta n=\pm1$
		$F_c=0.5$				
217	$HO+C_3H_8 \rightarrow H_2O+C_3H_7$	1.10×10^{-12}	±0.08	$8.0\times10^{-12}\exp(-590/T)$	240–300	±150
219	$HO+CH_3CH_2CH_2CH_3 \rightarrow$ products	2.4×10^{-12}	±0.10	$9.0\times10^{-12}\exp(-395/T)$	240–300	±200
221	$HO+CO \rightarrow H+CO_2$	1.3×10^{-13} (1+0.6 P/bar)	±0.1	$1.3\times10^{-13}[1+(0.6$ P/bar$)$	200–300	$\Delta\log k=\pm0.2$
221	$HO+CO+M \rightarrow HOCO+M$			$\times(300/T)^{1.0}]$		
222	$HO+HCHO \rightarrow H_2O+HCO$	9.2×10^{-12}	±0.10	$8.6\times10^{-12}\exp(20/T)$	240–300	±150
223	$HO+CH_3CHO \rightarrow H_2O+CH_3CO$	1.6×10^{-11}	±0.10	$5.6\times10^{-12}\exp(310/T)$	240–530	±200
224	$HO+C_2H_5CHO \rightarrow$ products	2.0×10^{-11}	±0.15			
225	$HO+CH_3CH_2CH_2CHO \rightarrow$ products	2.3×10^{-11}	±0.15	$5.2\times10^{-12}\exp(450/T)$	250–430	±300
226	$HO+(CHO)_2 \rightarrow H_2O+CHOCO$	1.1×10^{-11}	±0.3			
227	$HO+HOCH_2CHO \rightarrow H_2O+HOCH_2CO$	8.0×10^{-12}	±0.3			
	$\rightarrow H_2O+HOCHCHO$	2.0×10^{-12}	±0.3			
228	$HO+CH_3COCHO \rightarrow H_2O+CH_3COCO$	1.5×10^{-11}	±0.2			
229	$HO+CH_3COCH_3 \rightarrow H_2O+CH_2COCH_3$	1.9×10^{-13}	±0.15	$1.1\times10^{-12}\exp(-520/T)$	240–300	±200
230	$HO+CH_3C(O)CH_2CH_3 \rightarrow$ products	1.2×10^{-12}	±0.15	$1.3\times10^{-12}\exp(-25/T)$	240–300	±200
231	$HO+CH_3OH \rightarrow H_2O+CH_2OH$	7.9×10^{-13}	±0.15	$3.1\times10^{-12}\exp(-360/T)$	240–300	±200
	$\rightarrow H_2O+CH_3O$	1.4×10^{-13}	±0.15			
232	$HO+C_2H_5OH \rightarrow H_2O+CH_2CH_2OH$	1.6×10^{-13}	±0.15	$4.1\times10^{-12}\exp(-70/T)$	270–340	±200
	$\rightarrow H_2O+CH_3CHOH$	2.9×10^{-12}	±0.15			
	$\rightarrow H_2O+CH_3CH_2O$	1.6×10^{-13}	±0.15			
234	$HO+CH_3CH_2CH_2OH \rightarrow$ products	5.5×10^{-12}	±0.2			
235	$HO+CH_3CH(OH)CH_3 \rightarrow$ products	5.1×10^{-12}	±0.12	$2.7\times10^{-12}\exp(190/T)$	270–340	±200
236	$HO+CH_3CH_2CH_2CH_2OH \rightarrow$ products	8.1×10^{-12}	±0.2			
237	$HO+CH_3CH(OH)CH_2CH_3 \rightarrow$ products	8.9×10^{-12}	±0.3			
237	$HO+CH_3OCH_3 \rightarrow H_2O+CH_3OCH_2$	2.8×10^{-12}	±0.2	$5.8\times10^{-12}\exp(-220/T)$	240–300	±200

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

Page No.	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$^{a}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
238	$HO+CH_3COCH_2OH \rightarrow products$	3.0×10^{-12}		±0.3			
239	$HO+CH_3OOH \rightarrow H_2O+CH_2OOH$	1.9×10^{-12}		±0.2	1.0×10^{-12} exp(190/T)	220–430	±150
	$\rightarrow H_2O+CH_3OO$	3.6×10^{-12}		±0.2	1.9×10^{-12} exp(190/T)	220–430	±150
240	$HO+HCOOH \rightarrow products$	4.5×10^{-13}		±0.15	4.5×10^{-13}	290–450	±250
241	$HO+CH_3COOH \rightarrow products$	8×10^{-13}		±0.3			
241	$HO+C_2H_5COOH \rightarrow products$	1.2×10^{-12}		±0.2	1.2×10^{-12}	290–450	±300
242	$HO+CH_3ONO_2 \rightarrow products$	2.3×10^{-14}		$^{+0.5}_{-0.2}$	4.0×10^{-13} exp(−845/T)	220–300	±400
244	$HO+C_2H_5ONO_2 \rightarrow products$	1.8×10^{-13}		±0.3	6.7×10^{-13} exp(−395/T)	230–300	±400
245	$HO+1\text{-}C_3H_7ONO_2 \rightarrow products$	6×10^{-13}	(1 bar air)	±0.3			
246	$HO+2\text{-}C_3H_7ONO_2 \rightarrow products$	2.9×10^{-13}		±0.2	6.2×10^{-13} exp(−230/T)	230–300	±300
248	$HO+1\text{-}C_4H_9ONO_2 \rightarrow products$	1.7×10^{-12}		±0.2			
248	$HO+2\text{-}C_4H_9ONO_2 \rightarrow products$	9×10^{-13}		±0.3			
249	$HO+CH_3C(O)OONO_2 \rightarrow products$	$<3\times10^{-14}$					
250	$HO+CH_3COCH_2ONO_2 \rightarrow products$	$<1\times10^{-12}$					
250	$HO+HCN \rightarrow products$	3×10^{-14}	(1 bar)	±0.5	1.2×10^{-13} exp(−400/T) (1 bar)	290–440	±300
251	$HO+CH_3CN \rightarrow products$	2.2×10^{-14}	(1 bar)	±0.15	8.1×10^{-13} exp(−1080/T) (1 bar)	250–390	±200
252	$HO_2+CH_3O_2 \rightarrow O_2+CH_3OOH$	5.2×10^{-12}		±0.3	3.8×10^{-13} exp(780/T)	225–580	±500
254	$HO_2+HOCH_2O_2 \rightarrow O_2+HOCH_2OOH$ $\rightarrow O_2+HCOOH+H_2O$	1.2×10^{-11}		±0.3	5.6×10^{-15} exp(2300/T)	275–335	±1500
255	$HO_2+C_2H_5O_2 \rightarrow O_2+C_2H_5OOH$	7.7×10^{-12}		±0.2	3.8×10^{-13} exp(900/T)	200–500	±400
256	$HO_2+CH_3CO_3 \rightarrow O_2+CH_3C(O)OOH$	1.0×10^{-11}		±0.3	4.3×10^{-13} exp(1040/T)	250–370	±500
	$\rightarrow O_3+CH_3C(O)OH$	3.6×10^{-12}		±0.3			
257	$HO_2+HOCH_2CH_2O_2 \rightarrow products$	1.0×10^{-11}		±0.3			
258	$HO_2+CH_3OCH_2O_2 \rightarrow O_2+CH_3OCH_2OOH$ $\rightarrow O_2+CH_3OCHO+H_2O$	See data sheet					
259	$HO_2+CH_3COCH_2O_2 \rightarrow O_2+CH_3COCH_2OOH$	9.0×10^{-12}		±0.3			
259	$HO_2+HCHO \rightarrow HOCH_2OO$	7.9×10^{-14}		±0.3	9.7×10^{-15} exp(625/T)	275–333	±600
260	$HOCH_2OO \rightarrow HO_2+HCHO$	1.5×10^{2}	(k/s^{-1})	±0.3	2.4×10^{12} exp(−7000/T)	275–333	±2000
261	$NO_3+CH_4 \rightarrow HNO_3+CH_3$	$<1\times10^{-18}$					
262	$NO_3+C_2H_2 \rightarrow products$	$<1\times10^{-16}$					
262	$NO_3+C_2H_4 \rightarrow products$	2.1×10^{-16}		±0.2	3.3×10^{-12} exp(−2880/T)	270–340	±500
263	$NO_3+C_2H_6 \rightarrow HNO_3+C_2H_5$	$<1\times10^{-17}$					
264	$NO_3+C_3H_6 \rightarrow products$	9.5×10^{-15}		±0.2	4.6×10^{-13} exp(−1155/T)	290–430	±300
265	$NO_3+C_3H_8 \rightarrow HNO_3+C_3H_7$	$<7\times10^{-17}$					
266	$NO_3+n\text{-}C_4H_{10} \rightarrow products$	4.6×10^{-17}		±0.2	2.8×10^{-12} exp(−3280/T)	290–430	±400
267	$NO_3+HCHO \rightarrow HNO_3+HCO$	5.8×10^{-16}		±0.3			
268	$NO_3+CH_3CHO \rightarrow HNO_3+CH_3CO$	2.7×10^{-15}		±0.2	1.4×10^{-12} exp(−1860/T)	260–370	±500
269	$NO_3+CH_3COCH_3 \rightarrow HNO_3+CH_3COCH_2$	$<3\times10^{-17}$					
269	$NO_3+CH_3OH \rightarrow products$	1.3×10^{-16}		±0.5	9.4×10^{-13} exp(−2650/T)	250–370	±700
270	$NO_3+C_2H_5OH \rightarrow products$	$<2\times10^{-15}$					
271	$NO_3+CH_3CH(OH)CH_3 \rightarrow products$	1.3×10^{-15}		±0.3			

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

Page No.	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$[a]	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K[a]
272	$NO_3+CH_3CH(OH)CH_2CH_3\rightarrow$products	2.0×10^{-15}		±0.3			
273	$CH_3+O_2+M\rightarrow CH_3O_2+M$	1.0×10^{-30} [N_2]	(k_0)	±0.2	$1.0\times10^{-30}(T/300)^{-3.3}$ [N_2]	200–300	$\Delta n=\pm1$
		1.8×10^{-12}	(k_∞)	±0.3	$1.8\times10^{-12}(T/300)^{1.1}$	200–300	$\Delta n=\pm1$
		$F_c=0.27$					
275	$C_2H_5+O_2\rightarrow C_2H_4+HO_2$	3.8×10^{-15}	(1 bar air)	±0.5			
		1.9×10^{-14}	(0.133 bar air)	±0.5			
276	$C_2H_5+O_2+M\rightarrow C_2H_5O_2+M$	5.9×10^{-29} [N_2]	(k_0)	±0.3	$5.9\times10^{-29}(T/300)^{-3.8}$ [N_2]	200–300	$\Delta n=\pm1$
		7.8×10^{-12}	(k_∞)	±0.2	7.8×10^{-12}	200–300	$\Delta\log k=\pm0.2$
		$F_c=0.54$			$F_c=\{0.58\exp(-T/1250)$ $+0.42\exp(-T/183)\}$	200–300	
278	n-$C_3H_7+O_2+M\rightarrow n$-$C_3H_7O_2+M$	8×10^{-12}	(k_∞)	±0.2	8×10^{-12}	200–300	$\Delta\log k=\pm0.2$
278	i-$C_3H_7+O_2+M\rightarrow i$-$C_3H_7O_2+M$	1.1×10^{-11}	(k_∞)	±0.3	1.1×10^{-11}	200–300	$\Delta\log k=\pm0.3$
279	1-$C_4H_9+O_2+M\rightarrow1$-$C_4H_9O_2+M$	7.5×10^{-12}	(k_∞)	±0.5			
279	2-$C_4H_9+O_2+M\rightarrow2$-$C_4H_9O_2+M$	1.7×10^{-11}	(k_∞)	±0.5			
280	$CH_3COCH_2+O_2+M\rightarrow CH_3COCH_2O_2+M$	1.5×10^{-12}	(k_∞)	±0.5			
281	$HCO+O_2\rightarrow CO+HO_2$	5.2×10^{-12}		±0.15	5.2×10^{-12}	200–400	±150
282	$CH_3CO+O_2+M\rightarrow CH_3C(O)O_2+M$	3.2×10^{-12}	(k_∞)	±0.2	3.2×10^{-12}	220–300	$\Delta\log k=\pm0.2$
283	$CH_2OH+O_2\rightarrow HCHO+HO_2$	9.6×10^{-12}		±0.12			
284	$CH_3CHOH+O_2\rightarrow CH_3CHO+HO_2$	1.9×10^{-11}		±0.3			
284	$CH_2CH_2OH+O_2\rightarrow$products	3.0×10^{-12}		±0.3			
285	$CH_3O+O_2\rightarrow HCHO+HO_2$	1.9×10^{-15}		±0.2	$7.2\times10^{-14}\exp(-1080/T)$	298–610	±300
286	$C_2H_5O+O_2\rightarrow CH_3CHO+HO_2$	9.5×10^{-15}		±0.2	$6.0\times10^{-14}\exp(-550/T)$	290–420	±300
287	1-$C_3H_7O+O_2\rightarrow C_2H_5CHO+HO_2$	9.7×10^{-15}		±0.2	$1.4\times10^{-14}\exp(-110/T)$	220–310	±500
288	2-$C_3H_7O+O_2\rightarrow CH_3COCH_3+HO_2$	7.2×10^{-15}		±0.2	$1.4\times10^{-14}\exp(-210/T)$	210–390	±200
288	$CH_3CH_2CH_2CH_2O+O_2\rightarrow CH_3CH_2CH_2CHO+HO_2$	9.5×10^{-15}		±0.3	$6.0\times10^{-14}\exp(-550/T)$	290–400	±500
289	$CH_3CH_2CH_2CH_2O\rightarrow CH_2CH_2CH_2CH_2OH$	1.6×10^{5} (s^{-1})	(1 bar)	±0.5	$2.4\times10^{11}\exp(-4240/T)$ (1 bar)	295–400	±1000
290	$CH_3OCH_2O+O_2\rightarrow CH_3OCHO+HO_2$	See data sheets					
290	$CH_3OCH_2O+M\rightarrow CH_3OCHO+H+M$						
290	$CH_3COCH_2O+O_2\rightarrow CH_3COCHO+HO_2$	See data sheets					
290	$CH_3COCH_2O+M\rightarrow CH_3CO+HCHO+M$						
291	$CH_3CH(O)CH_2CH_3+M\rightarrow CH_3CHO+C_2H_5+M$	2.2×10^{4} (s^{-1})	(1 bar)	±0.3	$2\times10^{14}\exp(-6830/T)$ (1 bar)	300–500	±500
292	$CH_3+O_3\rightarrow$products	2.5×10^{-12}		±0.3	$5.1\times10^{-12}\exp(-210/T)$	240–400	±200
293	$CH_3O+NO+M\rightarrow CH_3ONO+M$	1.6×10^{-29} [N_2]	(k_0)	±0.1	$1.6\times10^{-29}(T/300)^{-3.5}$ [N_2]	200–400	$\Delta n=\pm0.5$
		3.6×10^{-11}	(k_∞)	±0.5	$3.6\times10^{-11}(T/300)^{-0.6}$	200–400	$\Delta n=\pm0.5$
		$F_c=0.6$					
293	$CH_3O+NO\rightarrow HCHO+HNO$	See data sheet					
295	$C_2H_5O+NO+M\rightarrow C_2H_5ONO+M$	2.2×10^{-28} [N_2]	(k_0)	±0.3	$2.2\times10^{-28}(T/300)^{-3.5}$ [N_2]	200–400	$\Delta n=\pm0.5$
		4.4×10^{-11}	(k_∞)	±0.3	4.4×10^{-11}	200–300	$\Delta n=\pm0.5$
		$F_c=0.6$					
295	$C_2H_5O+NO\rightarrow CH_3CHO+HNO$	See data sheet					
296	i-$C_3H_7O+NO+M\rightarrow i$-$C_3H_7ONO+M$	3.4×10^{-11}	(k_∞)	±0.3	3.4×10^{-11}	200–300	$\Delta n=\pm0.5$

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

Page No.	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$^{a}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
296	i-$C_3H_7O+NO \rightarrow CH_3COCH_3+HNO$	See data sheet					
297	$CH_3O+NO_2+M \rightarrow CH_3ONO_2+M$	9.0×10^{-29} [N_2]	(k_0)	±0.3	$9.0\times10^{-29}(T/300)^{-4.5}$ [N_2]	200–400	$\Delta n=\pm1$
		1.9×10^{-11}	(k_∞)	±0.3	1.9×10^{-11}	200–400	$\Delta n=\pm0.5$
		$F_c=0.44$					
297	$CH_3O+NO_2 \rightarrow HCHO+HONO$	See data sheet					
299	$C_2H_5O+NO_2+M \rightarrow C_2H_5ONO_2+M$	2.8×10^{-11}	(k_∞)	±0.3	2.8×10^{-11}	200–300	$\Delta n=\pm0.5$
299	$C_2H_5O+NO_2 \rightarrow CH_3CHO+HONO$	See data sheet					
299	1-$C_3H_7O+NO_2+M \rightarrow$ 1-$C_3H_7ONO_2+M$	3.6×10^{-11}	(k_∞)	±0.3			
300	2-$C_3H_7O+NO_2+M \rightarrow$ 2-$C_3H_7ONO_2+M$	3.5×10^{-11}	(k_∞)	±0.2	3.5×10^{-11}	200–300	$\Delta n=\pm0.5$
300	1-$C_3H_7O+NO_2 \rightarrow CH_3COCH_3+HONO$	See data sheet					
301	$CH_3O_2+NO \rightarrow CH_3O+NO_2$	7.5×10^{-12}		±0.05	$2.8\times10^{-12}\exp(285/T)$	200–430	±100
302	$C_2H_5O_2+NO \rightarrow C_2H_5O+NO_2$	9.0×10^{-12}		±0.1	$2.5\times10^{-12}\exp(380/T)$	200–410	±100
302	$C_2H_5O_2+NO(+M) \rightarrow C_2H_5ONO_2(+M)$	$\leqslant1.3\times10^{-13}$	(1 bar)				
303	$HOCH_2CH_2O_2+NO \rightarrow HOCH_2CH_2O+NO_2$	9×10^{-12}		±0.5			
303	n-$C_3H_7O_2+NO \rightarrow n$-$C_3H_7O+NO_2$	9.4×10^{-12}		±0.2	$2.9\times10^{-12}\exp(350/T)$	200–410	±100
303	n-$C_3H_7O_2+NO(+M) \rightarrow n$-$C_3H_7ONO_2(+M)$	1.9×10^{-13}	(1 bar)	±0.5			
304	i-$C_3H_7O_2+NO \rightarrow i$-$C_3H_7O+NO_2$	9.0×10^{-12}		±0.1	$2.7\times10^{-12}\exp(360/T)$	200–410	±100
304	i-$C_3H_7O_2+NO(+M) \rightarrow i$-$C_3H_7ONO_2(+M)$	3.8×10^{-13}	(1 bar)	±0.5			
305	$CH_3CO_3+NO \rightarrow CH_3CO_2+NO_2$	2.0×10^{-11}		±0.2	$7.8\times10^{-12}\exp(300/T)$	200–350	±250
306	$C_2H_5CO_3+NO \rightarrow C_2H_5CO_2+NO_2$	2.8×10^{-11}		±0.3	$1.2\times10^{-11}\exp(240/T)$	240–310	±500
307	$CH_3O_2+NO_2+M \rightarrow CH_3O_2NO_2+M$	2.5×10^{-30} [N_2]	(k_0)	±0.3	$2.5\times10^{-30}(T/300)^{-5.5}$ [N_2]	250–350	$\Delta n=\pm1$
		7.5×10^{-12}	(k_∞)	±0.3	7.5×10^{-12}	250–350	$\Delta n=\pm0.5$
		$F_c=0.36$					
308	$CH_3O_2NO_2+M \rightarrow CH_3O_2+NO_2+M$	6.8×10^{-19} [N_2]	(k_0/s^{-1})	±0.3	$9\times10^{-5}\exp(-9690/T)$ [N_2]	250–300	±500
		4.5	(k_∞/s^{-1})	±0.3	$1.1\times10^{16}\exp(-10560/T)$	250–300	±500
		$F_c=0.36$					
310	$C_2H_5O_2+NO_2+M \rightarrow C_2H_5O_2NO_2+M$	1.3×10^{-29} [N_2]	(k_0)	±0.3	$1.3\times10^{-29}(T/300)^{-6.2}$ [N_2]	200–300	$\Delta n=\pm1$
		8.8×10^{-12}	(k_∞)	±0.3	8.8×10^{-12}	200–300	$\Delta\log k=\pm0.3$
		$F_c=0.31$			$F_c=0.31$	250–300	
311	$C_2H_5O_2NO_2+M \rightarrow C_2H_5O_2+NO_2+M$	1.4×10^{-17} [N_2]	(k_0/s^{-1})	±0.5	$4.8\times10^{-4}\exp(-9285/T)$ [N_2]	250–300	±1000
		5.4	(k_∞/s^{-1})	±0.5	$8.8\times10^{15}\exp(-10440/T)$	250–300	±1000
		$F_c=0.31$			$F_c=0.31$	250–300	
312	$CH_3CO_3+NO_2+M \rightarrow CH_3CO_3NO_2+M$	2.7×10^{-28} [N_2]	(k_0)	±0.4	$2.7\times10^{-28}(T/300)^{-7.1}$ [N_2]	250–300	$\Delta n=\pm2$
		1.2×10^{-11}	(k_∞)	±0.2	$1.2\times10^{-11}(T/300)^{-0.9}$	250–300	$\Delta n=\pm1$
		$F_c=0.3$					
314	$CH_3CO_3NO_2+M \rightarrow CH_3CO_3+NO_2+M$	1.1×10^{-20} [N_2]	(k_0/s^{-1})	±0.4	$4.9\times10^{-3}\exp(-12100/T)$ [N_2]	300–330	±1000
		3.8×10^{-4}	(k_∞/s^{-1})	±0.3	$5.4\times10^{16}\exp(-13830/T)$	300–330	±300
		$F_c=0.3$					
315	$C_2H_5CO_3NO_2+M \rightarrow C_2H_5CO_3+NO_2+M$	4.4×10^{-4}	(k_∞/s^{-1})	±0.4	$2\times10^{15}\exp(-12800/T)$	300–315	±1000
316	$CH_3O_2+NO_3 \rightarrow CH_3O+NO_2+O_2$	1.3×10^{-12}		±0.3			
317	$C_2H_5O_2+NO_3 \rightarrow C_2H_5O+NO_2+O_2$	2.3×10^{-12}		±0.2			

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

Page No.	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$^{a}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
318	$CH_3O_2+CH_3O_2 \rightarrow CH_3OH+HCHO+O_2$ $\rightarrow 2CH_3O+O_2$ $\rightarrow CH_3OOCH_3+O_2$	3.7×10^{-13}	±0.12	1.1×10^{-13} exp(365/T)	200–400	±200
320	$CH_3O_2+CH_3C(O)O_2$					
	$\rightarrow CH_3O+CH_3CO_2+O_2$ $\rightarrow CH_3COOH+HCHO+O_2$	9.5×10^{-12}	0.15	1.8×10^{-12} exp(500/T)	200–350	±250
321	$CH_3O_2+CH_3COCH_2O_2$					
	$\rightarrow CH_3OH+CH_3COCHO+O_2$ $\rightarrow HCHO+CH_3COCH_2OH+O_2$ $\rightarrow CH_3O+CH_3COCH_2O+O_2$	3.8×10^{-12}	±0.3			
322	$HOCH_2O_2+HOCH_2O_2$					
	$\rightarrow HCOOH+CH_2(OH)_2+O_2$	7.0×10^{-13}	±0.3	5.7×10^{-14} exp(750/T)	270–330	±750
	$\rightarrow 2HOCH_2O+O_2$	5.5×10^{-12}	±0.3			
323	$C_2H_5O_2+C_2H_5O_2 \rightarrow C_2H_5OH+CH_3CHO+O_2$ $\rightarrow 2C_2H_5O+O_2$ $\rightarrow C_2H_5OOC_2H_5+O_2$	6.4×10^{-14}	±0.12	6.4×10^{-14}	250–450	$^{+300}_{-100}$
324	$C_2H_5O_2+CH_3C(O)O_2$					
	$\rightarrow C_2H_5O+CH_3CO_2+O_2$ $\rightarrow CH_3CHO+CH_3C(O)OH+O_2$	1.0×10^{-11}	±0.5			
325	$CH_3OCH_2O_2+CH_3OCH_2O_2$					
	$\rightarrow CH_3OCH_2OH+CH_3OCHO+O_2$	7×10^{-13}	±0.3			
	$\rightarrow 2CH_3OCH_2O+O_2$	1.4×10^{-12}	±0.3			
326	$CH_3C(O)O_2+CH_3C(O)O_2 \rightarrow 2CH_3C(O)O+O_2$	1.5×10^{-11}	±0.1	2.9×10^{-12} exp(500/T)	200–370	±200
327	$CH_3CO_3+CH_3COCH_2O_2$					
	$\rightarrow CH_3COOH+CH_3COCHO+O_2$ $\rightarrow CH_3CO_2+CH_3COCH_2O+O_2$	5.0×10^{-12}	±0.3			
328	$HOCH_2CH_2O_2+HOCH_2CH_2O_2$					
	$\rightarrow HOCH_2CH_2OH+HOCH_2CHO+O_2$	1.1×10^{-12}	±0.1	7.8×10^{-14} exp(1000/T)	250–450	±300
	$\rightarrow 2HOCH_2CH_2O+O_2$	1.1×10^{-12}	±0.1			
329	$n\text{-}C_3H_7O_2+n\text{-}C_3H_7O_2$					
	$\rightarrow n\text{-}C_3H_7OH+C_2H_5CHO+O_2$ $\rightarrow 2n\text{-}C_3H_7O+O_2$	3×10^{-13}	±0.5			
330	$i\text{-}C_3H_7O_2+i\text{-}C_3H_7O_2$					
	$\rightarrow i\text{-}C_3H_7OH+CH_3COCH_3+O_2$	4.4×10^{-16}	±0.3	1.6×10^{-12} exp($-2200/T$)	300–400	±300
	$\rightarrow 2i\text{-}C_3H_7O+O_2$	5.6×10^{-16}	±0.3			
331	$CH_3COCH_2O_2+CH_3COCH_2O_2$					
	$\rightarrow CH_3COCH_2OH+CH_3COCHO+O_2$	2.0×10^{-12}	±0.5			
	$\rightarrow 2CH_3COCH_2O+O_2$	6.0×10^{-12}	±0.3			

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

Page No.	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$^{a}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
332	$RCHOO+O_3\rightarrow RCHO+2O_2$	No recommendations (see data sheets)				
332	$RCHOO+H_2O\rightarrow$products					
332	$RCHOO+CO\rightarrow$products					
332	$RCHOO+HCHO\rightarrow$products					
332	$RCHOO+C_2H_4\rightarrow$products					
332	$RCHOO+NO\rightarrow RCHO+NO_2$					
332	$RCHOO+NO_2\rightarrow RCHO+NO_3$					
332	$RCHOO+SO_2\rightarrow$products					
332	$RCHOO+HCOOH\rightarrow$products					
335	$O_3+C_2H_2\rightarrow$products	1×10^{-20}	±1.0			
336	$O_3+C_2H_4\rightarrow$products	1.6×10^{-18}	±0.10	$9.1\times10^{-15}\exp(-2580/T)$	180–360	±100
338	$O_3+C_3H_6\rightarrow$products	1.0×10^{-17}	±0.10	$5.5\times10^{-15}\exp(-1880/T)$	230–370	±200
340	$F+CH_4+HF+CH_3$	6.7×10^{-11}	±0.15	$1.6\times10^{-10}\exp(-260/T)$	180–410	±200
341	$Cl+CH_4\rightarrow HCl+CH_3$	1.0×10^{-13}	±0.06	$6.6\times10^{-12}\exp(-1240/T)$	200–300	±200
343	$Cl+C_2H_2+M\rightarrow C_2H_2Cl+M$	6.1×10^{-30} [N_2] (k_0)	±0.3	$6.1\times10^{-30}(T/300)^{-3}$ [N_2]	200–300	$\Delta n=\pm1$
		2.0×10^{-10} (k_∞)	±0.3	2.0×10^{-10}	200–400	$\Delta n=\pm1$
		$F_c=0.6$				
344	$Cl+C_2H_4+M\rightarrow C_2H_4Cl+M$	1.7×10^{-29} [air] (k_0)	±0.5	$1.7\times10^{-29}(T/300)^{-3.3}$ [air]	250–300	$\Delta n=\pm1$
		3×10^{-10} (k_∞)	±0.3	3×10^{-10}	250–300	$\Delta n=\pm1$
		$F_c=0.6$				
346	$Cl+C_2H_6\rightarrow HCl+C_2H_5$	5.9×10^{-11}	±0.06	$8.3\times10^{-11}\exp(-100/T)$	220–600	±100
347	$Cl+C_3H_6+M\rightarrow C_3H_6Cl+M$	4.0×10^{-28} [N_2] (k_0)	±0.5			
		2.8×10^{-10} (k_∞)	±0.3			
349	$Cl+C_3H_8\rightarrow HCl+C_3H_7$	1.4×10^{-10}	±0.06	1.4×10^{-10}	200–700	±100
350	$Cl+n\text{-}C_4H_{10}\rightarrow HCl+C_4H_9$	2.2×10^{-10}	±0.06	2.2×10^{-10}	290–600	±100
351	$Cl+HCHO\rightarrow HCl+HCO$	7.3×10^{-11}	±0.06	$8.2\times10^{-11}\exp(-34/T)$	200–500	±100
352	$Cl+CH_3CHO\rightarrow HCl+CH_3CO$	7.2×10^{-11}	±0.15	7.2×10^{-11}	210–340	±300
353	$Cl+C_2H_5CHO\rightarrow$products	1.2×10^{-10}	±0.3			
353	$Cl+CH_3COCH_3\rightarrow HCl+CH_3COCH_2$	3.5×10^{-12}	±0.3			
354	$Cl+CH_3COCH_2CH_3\rightarrow$products	4.3×10^{-11}	±0.2			
355	$Cl+CH_3OH\rightarrow HCl+CH_2OH$	5.5×10^{-11}	±0.15	5.5×10^{-11}	200–580	±200
356	$Cl+C_2H_5OH\rightarrow$products	9.0×10^{-11}	±0.1			
356	$Cl+n\text{-}C_3H_7OH\rightarrow$products	1.5×10^{-10}	±0.2			
357	$Cl+i\text{-}C_3H_7OH\rightarrow$products	8.4×10^{-11}	±0.3			
358	$Cl+CH_3OOH\rightarrow$products	5.9×10^{-11}	±0.5			
358	$Cl+HCOOH\rightarrow$products	2.0×10^{-13}	±0.2			
359	$Cl+CH_3COOH\rightarrow$products	2.8×10^{-14}	±0.3			
360	$Cl+CH_3ONO_2\rightarrow$products	2.4×10^{-13}	±0.3			
360	$Cl+C_2H_5ONO_2\rightarrow$products	4.7×10^{-12}	±0.2			
361	$Cl+n\text{-}C_3H_7ONO_2\rightarrow$products	2.7×10^{-11}	±0.2			
362	$Cl+i\text{-}C_3H_7ONO_2\rightarrow$products	5.8×10^{-12}	±0.3			

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

Page No.	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta \log k_{298}$[a]	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K[a]
362	$Cl+1\text{-}C_4H_9ONO_2 \rightarrow$products	8.5×10^{-11}	±0.3			
363	$Cl+CH_3C(O)OONO_2 \rightarrow$products	$<2\times10^{-14}$				
363	$Cl+CH_3CN \rightarrow$products	1.2×10^{-14}	±0.3	$1.6\times10^{-11}\exp(-2140/T)$	270–350	±300
364	$Br+HCHO \rightarrow HBr+HCO$	1.1×10^{-12}	±0.15	$1.7\times10^{-11}\exp(-800/T)$	220–480	±250
365	$Br+CH_3CHO \rightarrow HBr+CH_3CO$	3.9×10^{-12}	±0.2	$1.3\times10^{-11}\exp(-360/T)$	250–400	±200
366	$HCHO+h\nu \rightarrow$products	See data sheet				
368	$CH_3CHO+h\nu \rightarrow$products	See data sheet				
370	$C_2H_5CHO+h\nu \rightarrow$products	See data sheet				
372	$(CHO)_2+h\nu \rightarrow$products	See data sheet				
374	$CH_3COCHO+h\nu \rightarrow$products	See data sheet				
376	$CH_3COCH_3+h\nu \rightarrow$products	See data sheet				
378	$CH_3COC_2H_5+h\nu \rightarrow$products	See data sheet				
379	$CH_3OOH+h\nu \rightarrow$products	See data sheet				
380	$CH_3ONO_2+h\nu \rightarrow$products	See data sheet				
381	$C_2H_5ONO_2+h\nu \rightarrow$products	See data sheet				
383	$n\text{-}C_3H_7ONO_2+h\nu \rightarrow$products	See data sheet				
384	$i\text{-}C_3H_7ONO_2+h\nu \rightarrow$products	See data sheet				
385	$1\text{-}C_4H_9ONO_2+h\nu \rightarrow$products	See data sheet				
387	$2\text{-}C_4H_9ONO_2+h\nu \rightarrow$products	See data sheet				
388	$CH_3O_2NO_2+h\nu \rightarrow$products	See data sheet				
389	$CH_3C(O)OONO_2+h\nu \rightarrow$products	See data sheet				

[a] The cited uncertainty is an expanded uncertainty corresponding approximately to a 95% confidence limit.

3. Guide to the Data Sheets

3.1. Gas-Phase Reactions

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

3.1.1. Thermal Reactions

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

The available kinetic data on the reactions are summarized under three headings: (i) Absolute Rate Coefficients, (ii) Relative Rate Coefficients, and (iii) Reviews and Evaluations. Under headings (i) and (ii), we include new data which have been published since the last complete IUPAC evaluation[6] as well as the data used in deriving the preferred values. Under heading (iii) are listed the preferred rate data from the most recently published NASA evaluation[8] available at the date of submission of this evaluation and our own IUPAC evaluations, together with data from any new review or evaluation source. Under all three of the headings above, the data are presented as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in a temperature-dependent form over a stated temperature range. For bimolecular reactions, the temperature dependence is usually expressed in the normal Arrhenius form, $k=A\exp(-B/T)$, where $B=E/R$. For a few bimolecular reactions, we have listed temperature dependences in the alternative form, $k=A'T^n$ or $CT^n\exp(-D/T)$, where the original authors have found this to give a better fit to their data. For pressure-dependent combination and dissociation reactions, the non-Arrhenius temperature dependence is used. This is discussed more fully in a subsequent section of the Introduction.

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

A - absorption
AS - absorption spectroscopy
CIMS - chemical ionization mass spectroscopy/spectrometric
CL - chemiluminescence
DF - discharge flow
EPR - electron paramagnetic resonance
F - flow system
FP - flash photolysis
FTIR - Fourier transform infrared
FTS - Fourier transform spectroscopy
GC - gas chromatography/gas chromatographic
HPLC - high-performance liquid chromatography
IR - infrared
LIF - laser induced fluorescence
LMR - laser magnetic resonance
LP - laser photolysis
MM - molecular modulation
MS - mass spectrometry/mass spectrometric
P - steady state photolysis
PLP - pulsed laser photolysis
PR - pulse radiolysis
RA - resonance absorption
RF - resonance fluorescence
RR - relative rate
S - static system
SH - shock heating (in a shock tube)
TDLS - tunable diode laser spectroscopy
UV - ultraviolet
UVA - ultraviolet absorption
VUVA - vacuum ultraviolet absorption

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

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

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

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

3.1.2. Conventions Concerning Rate Coefficients

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

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

$$\frac{-1/2\,d[A]}{dt}=\frac{d[B]}{dt}=\frac{d[C]}{dt}=k[A]^2.$$

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.

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

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

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

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

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 coefficient expressed as the product of a third-order rate coefficient and the third body concentration, which is expressed in molecule cm^{-3}. The transition between the third-order and the second-order range is represented by a reduced falloff expression of k_0/k_∞ as a function of $[M]/[M]_c$, 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_∞. The dependence of *k* on [M] in general is complicated and has to be analyzed by unimolecular rate theory. For moderately complex molecules at not too high temperatures, however, a simple approximate relationship holds:

$$k=\frac{k_0k_\infty}{k_0+k_\infty}F=k_0\frac{1}{1+k_0/k_\infty}F=k_\infty\frac{k_0/k_\infty}{1+k_0/k_\infty}F$$

where the first factors at the right-hand side represent the Lindemann–Hinshelwood expression, and the additional broadening factor *F*, at not too high temperature, is approximately given by[9–11]

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

With increasing temperature, a better representation is obtained[9–11] by replacing $[\log(k_0/k_\infty)]^2$ by $[\log(k_0/k_\infty)/N]^2$ with $N=\{0.75-1.27\log F_c\}$. In this way the three quantities k_0, k_∞, and F_c characterize the falloff curve for the present application.

Alternatively, the three quantities k_∞, $[M]_c$, and F_c (or k_0, $[M]_c$, and F_c) can be used. The temperature dependence of F_c, which is sometimes significant, can be estimated by the procedure of Troe.[9–11] The results can usually be represented approximately by the equation:

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

Whereas the two first terms are of importance for atmospheric conditions, the last term in most cases becomes relevant only at much higher temperatures. In Ref. 2, for simplicity $a=1$ and $T^{**}=4T^{*}$ were adopted. Often $F_c=\exp(-T/T^{*})$ is sufficient for low-temperature conditions. With molecules of increasing complexity, additional broadening of the falloff curves may have to be taken into account.[9–11] For simplicity these effects are neglected in the present evaluation. An even simpler policy was chosen in Ref. 8 where a temperature independent standard value of $F_c=0.6$ was adopted. This choice, however, often oversimplifies the representation.

If a given falloff curve is fitted, changes in F_c require changes in the limiting k_0 and k_∞ values. For the purpose of this evaluation, this is irrelevant, if the preferred k_0 and k_∞ are used consistently together with the preferred F_c values. If the selected value of F_c is too large, the values of k_0 and k_∞, obtained by fitting the falloff expression to the experimental data, are underestimated. Theoretical predictions of F_c have been derived from rigid Rice–Ramsperger–Kassel–Marcus (RRKM)-type models including weak collision effects.[9–11]

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

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

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

$$k_0(M_1)/[M_1]:k_0(M_2)/[M_2].$$

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

For reactions involving parallel rearrangement/dissociation and stabilization channels from a common activated complex,

$$\begin{array}{c} A+B \rightleftarrows AB^* \rightarrow C+D \\ \downarrow M \\ AB \end{array}$$

then providing that dissociation of AB^* back to reactants dominates over dissociation of AB^* to C+D in the low pressure limit, a Lindemann–Hinshelwood treatment leads to

$$k_2(M)=k_{02}k_1(M)/k_{01}$$

where $k_2(M)$ is the effective second-order rate coefficient for formation of C+D at a given third-body concentration [M], $k_1(M)$ is the effective second-order rate coefficient for formation of AB at the same concentration of M, and k_{01} is the second-order limiting low-pressure rate coefficient at the same concentration of M (i.e., incorporating [M]).

3.1.4. Photochemical Reactions

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

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

The next table lists the preferred absorption cross-section data and the preferred quantum yields at appropriate wavelength intervals. For absorption cross-sections the intervals are usually 1, 5, or 10 nm. Any temperature dependence of the absorption cross-sections is also given where possible. The aim in presenting these preferred data is to provide a basis for calculating atmospheric photolysis rates. For absorption continua the temperature dependence is often represented by Sulzer–Wieland type expressions.[12]

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

3.1.5. Conventions Concerning Absorption Cross Sections

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

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

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

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

3.1.6. Assignment of Uncertainties

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 $E/R=H\pm G$. D and G are expanded uncertainties corresponding approximately to a 95% confidence limit.

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

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

The assignment of these absolute uncertainties in k and E/R is a subjective assessment of the evaluators. They are not determined by a rigorous, statistical analysis of the data base, which is generally too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the techniques, the difficulties of the experimental measurements, the potential for systematic errors, and the number of studies conducted and their agreement or lack thereof. 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 uncertainties which are difficult to detect. This is hardly surprising since, unlike molecular reactions, it is not always possible to study atomic and free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise.

The arbitrary assignment of uncertainties 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 carried out and the number of different techniques used. On the whole, our assessment of uncertainty limits tends toward 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 uncertainty limits of a factor of 2 are appropriate.

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

3.2. Acknowledgments

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3.3. References for the Introduction

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

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

[3] D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data **13**, 1259 (1984).

[4] R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, J. Phys. Chem. Ref. Data **18**, 881 (1989).

[5] R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, J. Phys. Chem. Ref. Data **21**, 1125 (1992).

[6] R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. Rossi, and J. Troe, J. Phys. Chem. Ref. Data **26**, 521 (1997).

[7] R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe, J. Phys. Chem. Ref. Data **26**, 1329 (1997).

[8] W. B. DeMore, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, NASA Panel for Data Evaluation, Evaluation Number 12, JPL Publication 97-4 (1997). (Contains references to the previous Evaluations, Numbers 1-11 in this series.)

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

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

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

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

4. Gas-Phase Reaction—Data Sheets

4.1. Organic Species

$$\begin{aligned} O + CH_3 &\rightarrow HCHO + H \qquad (1)\\ &\rightarrow HCO + H_2 \qquad (2)\\ &\rightarrow CO + H_2 + H \qquad (3)\\ &\rightarrow OH + CH_2 \qquad (4) \end{aligned}$$

$\Delta H°(1) = -286.2\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta H°(2) = -352.5\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta H°(3) = -288.1\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta H°(4) = 34.1\ \mathrm{kJ \cdot mol^{-1}}$

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

k/cm^3 molecule^{-2} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.17) \times 10^{-10}$	1700–2300	Bhaskaran, Franck, and Just, 1979[1]	SH-RA (a)
$(1.14 \pm 0.29) \times 10^{-10}$	295	Plumb and Ryan, 1982[2]	DF-MS (b)
$(1.4 \pm 0.3) \times 10^{-10}$	294–900	Slagle, Sarzynski, and Gutman, 1987[3]	F-MS (c)
$k_1 = (1.1 \pm 0.4) \times 10^{-10}$	298	Zellner *et al.*, 1988[4]	LP-LIF (d)
$(1.3 \pm 0.2) \times 10^{-10}$	300	Oser *et al.*, 1991[5]	DF-MS (e)
$(9.4 \pm 3.0) \times 10^{-11}$	~298	Seakins and Leone, 1992[6]	PLP-FTIR (f)
$(1.4 \pm 0.3) \times 10^{-10}$	1609–2002	Lim and Michael, 1993[7]	SH-RA (g)
Branching Ratios			
$k_1/k > 0.85$	300	Niki, Daby, and Weinstock, 1968[8]	DF-MS (h)
$k_2/k \leqslant 0.2$	300	Hoyermann and Sievert, 1979[9]	F-MS (i)
Reviews and Evaluations			
1.4×10^{-10}	300–2500	Baulch *et al.*, 1992[10]	(j)
1.1×10^{-10}	260–350	NASA, 1997[11]	(k)
1.4×10^{-10}	290–900	IUPAC, 1997[12]	(j)

Comments

(a) Decomposition of C_2H_6–O_2 mixtures in a shock tube. k was derived from computer simulation of [O] and [H] profiles determined by RA.

(b) Discharge flow system with MS detection of O and CH_3, k was determined from the decay of $[CH_3]$ with $[O] \gg [CH_3]$.

(c) Flow system with generation of CH_3 radicals and $O(^3P)$ atoms from simultaneous *in situ* photolysis of CH_3COCH_3 and SO_2, and determination of $[CH_3]$ and [O] by photoionization MS. Experiments were performed under conditions such that $[O]/[CH_3] > 20$, and rate coefficients were determined from the decay of CH_3 radicals. The rate coefficient k was found to be independent of pressure over the range 1.3–15 mbar (1–11 Torr), and its value was confirmed by measurement of the rate of formation of HCHO. HCO and CH_2 were not detected as products but the analytical system could not detect CO or H_2.

(d) Laser photolysis at 193 nm of flowing mixtures of N_2–N_2O–$(CH_3)_2N_2$. k was determined from the rate of formation of HCHO [using laser-induced fluorescence (LIF)] with $[O] > [CH_3]$. Mass balance estimates indicated that channel (1) predominates.

(e) Discharge flow system with generation of CH_3 from $F + CH_4$ in He–O_2 mixtures at pressures of 0.25–1.0 mbar (0.17–0.78 Torr). k was determined from the decay of $[CH_3]$ by MS with $[O]/[CH_3] > 10$.

(f) Obtained from the rate of formation of HCHO product by monitoring the C–H stretch emission by Fourier transform infrared spectroscopy (FTIR).

(g) Shock heating of CH_3Cl in Ar coupled with laser photolysis of SO_2. k was determined from computer simulation of [O] profiles measured by RA.

(h) DF-MS study of $O + C_2H_4$ reaction in which CH_3 is a product. HCHO assumed to arise from channel (1).

(i) Discharge flow system with CH_3 being generated from $F + CH_4$ and O from a microwave discharge. Electron impact MS analysis of HCO and HCHO. No evidence found for channel (4).

(j) Based on the data of Slagle *et al.*[3]

(k) k_{298} is the weighted average of the measurements of Washida and Bayes,[13] Washida[14] and Plumb and

Ryan,[2] and E/R is based on the results of Washida and Bayes.[13]

Preferred Values

$k = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–900 K.

Reliability

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

Comments on Preferred Values

The recommended value of k is the mean of the results of Plumb and Ryan,[2] Slagle *et al.*,[3] Zellner *et al.*,[4] Oser *et al.*,[5] and Seakins and Leone,[6] which are in excellent agreement. The data of Bhaskaran *et al.*[1] and Lim and Michael[7] indicate that the rate coefficient is independent of temperature up to at least 2300 K.

While there is evidence that channel (1) is predominant and that channel (4) does not appear to occur, the recommendation of values of the branching ratios requires more quantitative data. In this regard Seakins and Leone[6] have carried out pulsed laser photolysis studies of the $O+CH_3$ reaction and have observed excited HCHO and CO products by time-resolved FTIR spectroscopy. It was further shown[6] that CO was a primary product of the reaction, with an overall branching ratio for CO formation of 0.40±0.10, but it was not possible to establish the detailed pathways for CO formation.

References

[1] K. A. Bhaskaran, P. Franck, and Th. Just, *Proceedings of the 12th Symposium on Shock Tubes and Waves* (Magnes Press, Jerusalem, 1980), p. 503.
[2] I. C. Plumb and K. R. Ryan, Int. J. Chem. Kinet **14**, 861 (1982).
[3] I. R. Slagle, D. Sarzynski, and D. Gutman, J. Phys. Chem. **91**, 4375 (1987).
[4] R. Zellner, D. Hartmann, J. Karthäuser, D. Rhäsa, and G. Weibring, J. Chem. Soc. Faraday Trans. 2 **84**, 549 (1988).
[5] H. Oser, D. Walter, N. D. Stothard, O. Grotheer, and H. H. Grotheer, Chem. Phys. Lett. **181**, 521 (1991).
[6] P. W. Seakins and S. R. Leone, J. Phys. Chem. **96**, 4478 (1992).
[7] K. P. Lim and J. V. Michael, J. Chem. Phys. **98**, 3919 (1993).
[8] H. Niki, E. E. Daby, and B. Weinstock, J. Chem. Phys. **48**, 5729 (1968).
[9] K. Hoyermann and R. Sievert, *17th Symposium (International) Combustion* (The Combustion Institute, Pittsburgh, 1979), p. 517.
[10] D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Frank, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, J. Phys. Chem. Ref. Data **21**, 411 (1992).
[11] NASA Evaluation No. 12, 1997 (see references in Introduction).
[12] IUPAC, Supplement V, 1997 (see references in Introduction).
[13] N. Washida and K. D. Bayes, Int. J. Chem. Kinet. **8**, 777 (1976).
[14] N. Washida, J. Chem. Phys. **73**, 1665 (1980).

$$\begin{aligned} O(^1D) + CH_4 &\rightarrow HO + CH_3 && (1) \\ &\rightarrow CH_3O \text{ or } CH_2OH + H && (2) \\ &\rightarrow HCHO + H_2 && (3) \end{aligned}$$

$\Delta H^\circ(1) = -178.4$ kJ·mol^{-1}
$\Delta H^\circ(2) = -128.9$ kJ·mol^{-1} or -163.9 kJ·mol^{-1}
$\Delta H^\circ(3) = -472.7$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.3 \pm 0.2) \times 10^{-10}$	298	Davidson *et al.*, 1976[1]	PLP (a)
$(1.4 \pm 0.4) \times 10^{-10}$	200–350	Davidson *et al.*, 1977[2]	PLP (a)
$(1.57 \pm 0.13) \times 10^{-10}$	295	Amimoto *et al.*, 1979[3]	PLP-RA (b)
Branching Ratios			
$k_1/k \sim 0.9$	295	Lin and DeMore, 1973[4]	P-GC (c)
$k_3/k \approx 0.09$	295		
$k_1/k = (0.90 \pm 0.02)$	298	Jayanty, Simonaitis, and Heicklen, 1976[5]	P-GC (d)
$k_3/k = (0.11 \pm 0.02)$	298		
$k_1/k = 0.8$	293	Addison, Donovan, and Garraway, 1979[6]	FP-AS (e)
$k_3/k_2 < 0.25$	—	Casavecchia *et al.*, 1980[7]	(f)
$k_1/k = (0.75 \pm 0.08)$	—	Sataypal *et al.*, 1989[8]	PLP-LIF (g)
$k_2/k = (0.25 \pm 0.08)$	—		
$k_2/k = (0.15 \pm 0.03)$	—	Matsumi *et al.*, 1993[9]	PLP-LIF (g)
Reviews and Evaluations			
$k = 1.5 \times 10^{-10}$	200–350	NASA, 1997[10]	(h)
$k_1/k = 0.75$	298		(i)
$k_2/k = 0.20$	298		(i)
$k_3/k = 0.05$	298		(i)
$k = 1.5 \times 10^{-10}$	200–350	IUPAC, 1997[11]	(j)
$k_1/k = 0.9$	200–350		(k)
$k_3/k = 0.1$	200–350		(k)

Comments

(a) Pulsed laser photolysis of O_3 at 266 nm. $O(^1D)$ atoms were monitored by time-resolved emission from the transition $O(^1D) \rightarrow O(^3P)$ at 630 nm.

(b) Pulsed laser photolysis at 248 nm of O_3–CH_4–He mixtures with time-resolved measurement of $O(^3P)$ atoms by resonance absorption.

(c) Photolysis of N_2O–CH_4 mixtures at 184.9 nm with end-product analysis by GC.

(d) Photolysis of N_2O–CH_4–O_2 mixtures at 216 nm with measurement of H_2 by GC.

(e) Flash photolysis of O_3 at 200–300 nm with [OH] monitored by AS at 308.15 nm.

(f) Molecular beam study with MS detection of CH_3O or CH_2OH. Experimental temperature not stated.

(g) Pulsed laser photolysis of O_3 at 248.4 nm with LIF determination of [H]. Experimental temperature not stated.

(h) Total rate coefficient k was based on the data of Davidson *et al.*,[1,2] and Amimoto *et al.*,[3] with E/R from Davidson *et al.*[2]

(i) Based on the results of Lin and DeMore,[4] Addison *et al.*,[6] Casavecchia *et al.*,[7] Satyapal *et al.*,[8] and Matsumi *et al.*[9]

(j) See Comments on Preferred Values.

(k) Based on the results of Lin and DeMore[4] and Jayanty *et al.*[5]

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

$k = 1.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–350 K.

$k_1/k = 0.75$ at 298 K.
$k_2/k = 0.20$ at 298 K.
$k_3/k = 0.05$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta k_1/k = \pm 0.15$ at 298 K.
$\Delta k_2/k = \pm 0.07$ at 298 K.
$\Delta k_3/k = \pm 0.05$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred value of k at 298 K is the mean of the results of Davidson *et al.*[2] and Amimoto *et al.*,[3] and the temperature dependence is that from Davidson *et al.*[2]

The branching ratios are based on the measurements of Lin and DeMore,[4] Jayanty *et al.*,[5] Addison *et al.*,[6] Casavecchia *et al.*,[7] Satyapal *et al.*,[8] and Matsumi *et al.*[9] In addition, the experiments of Wine and Ravishankara,[12] Matsumi *et al.*,[9] and Takahashi *et al.*[13] have shown that the yield of $O(^3P)$ atoms is small or zero. The 248 nm pulsed laser photolysis study[14] of O_3–CH_4 mixtures with low-pressure FTIR emission spectroscopy to monitor the HO* product, has provided evidence that the partitioning of energy in the vibrationally excited HO radical (up to $n=4$, the maximum allowable based on the energetics of the reaction) is nonstatistical.

References

[1] J. A. Davidson, C. M. Sadowski, H. I. Schiff, G. E. Streit, C. J. Howard, D. A. Jennings, and A. L. Schmeltekopf, J. Chem. Phys. **64**, 57 (1976).

[2] J. A. Davidson, H. I. Schiff, G. E. Streit, J. R. McAfee, A. L. Schmeltekopf, and C. J. Howard, J. Chem. Phys. **67**, 5021 (1977).

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

[4] C. L. Lin and W. B. DeMore, J. Phys. Chem. **77**, 863 (1973).

[5] R. K. M. Jayanty, R. Simonaitis, and J. Heicklen, Int. J. Chem. Kinet. **8**, 107 (1976).

[6] M. C. Addison, R. J. Donovan, and J. Garraway, J. Chem. Soc. Faraday Discuss **67**, 286 (1979).

[7] P. Casavecchia, R. J. Buss, S. J. Sibener, and Y. T. Lee, J. Chem. Phys. **73**, 6351 (1980).

[8] S. Stayapal, J. Park, R. Bersohn, and B. Katz, J. Chem. Phys. **91**, 6873 (1989).

[9] Y. Matsumi, K. Tonokura, Y. Inagaki, and M. Kawasaki, J. Phys. Chem. **97**, 6816 (1993).

[10] NASA Evaluation No. 12, 1997 (see references in Introduction).

[11] IUPAC, Supplement V, 1997 (see references in Introduction).

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

[13] K. Takahashi, R. Wada, Y. Matsumi, and M. Kawasaki, J. Phys. Chem. **100**, 10145 (1996).

[14] P. M. Aker, J. J. A. O'Brien, and J. J. Sloan, J. Chem. Phys. **84**, 745 (1986).

$HO + CH_4 \rightarrow H_2O + CH_3$

$\Delta H^\circ = -59.9\ \mathrm{kJ\cdot mol^{-1}}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.3\pm0.9)\times10^{-12}$	1234±15	Bott and Cohen, 1989[1]	SH-RA
$1.59\times10^{-20}\ T^{2.84}\exp(-978/T)$	223–420	Vaghjiani and Ravishankara, 1991[2]	PLP-LIF
6.35×10^{-15}	298		
$4.0\times10^{-12}\exp[-(1944\pm114)/T]$	278–378	Finlayson-Pitts *et al.*, 1992[3]	DF-RF
5.87×10^{-15}	298		
$9.65\times10^{-20}\ T^{2.58}\exp(-1082/T)$	293–800	Dunlop and Tully, 1993[4]	PLP-LIF (a)
$(5.62\pm0.43)\times10^{-15}$	293		
$2.56\times10^{-12}\exp[-(1765\pm146)/T]$	233–343	Mellouki *et al.*, 1994[5]	PLP-LIF
$(6.34\pm0.88)\times10^{-15}$	298		
$1.89\times10^{-20}\ T^{2.82}\exp[-(987\pm6)/T]$	195–296	Gierczak *et al.*, 1997[6]	PLP-LIF/ FP-LIF (b)
$(6.40\pm0.38)\times10^{-15}$	298		
Reviews and Evaluations			
$2.45\times10^{-12}\exp(-1775/T)$	220–300	NASA, 1997[7]	(c)
$9.65\times10^{-20}\ T^{2.58}\exp(-1082/T)$	223–1234	Atkinson, 1997[8]	(d)
$2.3\times10^{-12}\exp(-1765/T)$	240–300	IUPAC, 1997[9]	(e)

Comments

(a) The temperature-dependent expression cited[4] is that for the rate coefficients of Dunlop and Tully[4] ($T=293-800$ K) combined with those of Vaghjiani and Ravishankara[2] ($T=223-420$ K) and as such covers the temperature range 223–800 K.[4]

(b) The temperature-dependent expression cited is that for the rate coefficients of Gierczak *et al.*[6] ($T=195-296$ K) combined with those of Vaghjiani and Ravishankara[2] ($T=223-420$ K) obtained using a similar technique, and therefore covers the temperature range 195–420 K.

(c) The 298 K rate coefficient was based on the absolute rate coefficient data of Vaghjiani and Ravishankara,[2] Finlayson-Pitts *et al.*,[3] Dunlop and Tully,[4] Saunders *et al.*,[10] Mellouki *et al.*,[5] and Gierczak *et al.*,[6] and the temperature dependence was derived from those of Vaghjiani and Ravishankara,[2] Finlayson-Pitts *et al.*,[3] Dunlop and Tully,[4] Mellouki *et al.*,[5] and Gierczak *et al.*[6] at temperatures <300 K.

(d) Derived from the absolute rate coefficient data of Dunlop and Tully[4] and Vaghjiani and Ravishankara.[2]

(e) Derived from the absolute rate coefficient data of Dunlop and Tully[4] and Vaghjiani and Ravishankara.[2] The temperature-dependent expression obtained by Dunlop and Tully[4] from a fit of their data and those of Vaghjiani and Ravishankara[2] to the three-parameter equation $k = CT^n \exp(-D/T)$, of $k = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T)$ cm^3 molecule^{-1} s^{-1} over the range 223–800 K was accepted. The preferred Arrhenius expression, $k = A \exp(-B/T)$, was centered at 265 K and was derived from the three-parameter equation with $A = Ce^nT^n$ and $B = D + nT$.

Preferred Values

$k = 6.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.15 \times 10^{-12} \exp(-1735/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

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

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

Comments on Preferred Values

The absolute rate coefficients of Vaghjiani and Ravishankara,[2] Finlayson-Pitts *et al.*,[3] Dunlop and Tully,[4] Mellouki *et al.*,[5] and Gierczak *et al.*[6] are in good agreement. However, over the temperature range ~250–420 K these rate coefficients of Vaghjiani and Ravishankara,[2] Finlayson-Pitts *et al.*,[3] Dunlop and Tully,[4] Mellouki *et al.*,[5] and Gierczak *et al.*[6] are ~20% lower than most of the previously reported absolute rate coefficients.[11]

The preferred values are derived from the absolute rate coefficient data of Vaghjiani and Ravishankara[2] and Gierczak *et al.*,[6] both conducted over significant, and overlapping, temperature ranges. The temperature-dependent expression obtained by Gierczak *et al.*[6] from a fit of their data[6] and those of Vaghjiani and Ravishankara[2] to the three-parameter equation $k = CT^n \exp(-D/T)$ is accepted, of $k = 1.89 \times 10^{-20} T^{2.82} \exp(-987/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 223–420 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$ is centered at 265 K and is derived from the three-parameter equation with $A = Ce^nT^n$ and $B = D + nT$. The recommended three-parameter expression leads to calculated rate coefficients at 800 and 1234 K which are within 12% and 3%, respectively, of the values measured by Dunlop and Tully[4] at 800 K and Bott and Cohen at 1234 K.[1]

The preferred values differ slightly from our previous recommendation, IUPAC, 1997[9] which was based on the temperature-dependent expression obtained by Dunlop and Tully[4] from a fit of their data[4] and those of Vaghjiani and Ravishankara.[2] The present three-parameter recommendation yields rate coefficients which are 13% higher at 195 K, 6% higher at 298 K, 5% higher at 400–500 K, 10% higher at 800 K and 17% higher at 1234 K than those calculated from our previous recommendation, IUPAC, 1997.[9]

References

[1] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **21**, 485 (1989).

[2] G. L. Vaghjiani and A. R. Ravishankara, Nature (London) **350**, 406 (1991).

[3] B. J. Finlayson-Pitts, M. J. Ezell, T. M. Jayaweera, H. N. Berko, and C. C. Lai, Geophys. Res. Lett. **19**, 1371 (1992).

[4] J. R. Dunlop and F. P. Tully, J. Phys. Chem. **97**, 11148 (1993).

[5] A. Mellouki, S. Téton, G. Laverdet, A. Quilgars, and G. Le Bras, J. Chim. Phys. **91**, 473 (1994).

[6] T. Gierczak, R. K. Talukdar, S. C. Herndon, G. L. Vaghjiani, and A. R. Ravishankara, J. Phys. Chem. A **101**, 3125 (1997).

[7] NASA Evaluation No. 12, 1997 (see references in Introduction).

[8] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

[9] IUPAC, Supplement V, 1997 (see references in Introduction).

[10] S. M. Saunders, K. J. Hughes, M. J. Pilling, D. L. Baulch, and P. L. Smurthwaite, Proc. SPIE **1715**, 88 (1993).

[11] R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

$HO + C_2H_2 + M \rightarrow C_2H_2OH + M$

$\Delta H° = -147$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3\pm1)\times10^{-30}$ $(T/300)^{1.0}$ [Ar]	297–429	Perry and Williamson, 1982[1]	FP-RF (a)
$(6\pm3)\times10^{-30}$ [He]	298	Hack *et al.*, 1983[2]	DF-EPR (b)
$(2.5\pm0.3)\times10^{-30}$ [Ar]	295	Schmidt *et al.*, 1985[3]	PLP-LIF (c)
5×10^{-30} [N$_2$]	298	Wahner and Zetzsch, 1985[4]	PLP-A (d)
$(4.1\pm1.6)\times10^{-30}$ [N$_2$]	298	Bohn, Siese, and Zetzsch, 1996[5]	PLP-A (e)
4.3×10^{-29} $(T/300)^{-3.1}$ $\exp(-910/T)$ [He]	300–814	Fulle *et al.*, 1997[6]	PLP-LIF (f)
2.1×10^{-30} [He]	298		
Reviews and Evaluations			
5.6×10^{-30} [Ar]	228–300	Smith, Fairchild, and Crosley, 1984[7]	(g)
5×10^{-30} $(T/298)^{-1.5}$ [N$_2$]	230–500	Atkinson, 1989[8]	(h)
5.5×10^{-30} [air]	200–300	NASA, 1997[9]	(i)
5×10^{-30} $(T/300)^{-1.5}$ [N$_2$]	200–300	IUPAC, 1997[10]	(j)

Comments

(a) Photolysis of H_2O–C_2H_2 mixtures with Ar diluent at between 26 and 530 mbar. Pressure dependence observed in agreement with earlier work.[11,12] Evaluation of the falloff curve with $F_c = 0.5$.

(b) Pressures around 2.6 mbar were used. By the use of data from Ref. 1 and $F_c = 0.5$, a falloff analysis of the measured k leads to the given k_0 value.

(c) Experiments in He, Ar, and N_2 at pressures between 1 and 1000 mbar (in Ar). Construction of falloff curve with $F_c = 0.6$ leading to $k_\infty = (8.3\pm0.8)\times10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(d) Experiments in N_2 over the range 20–1000 mbar. Falloff curve constructed with $F_c = 0.6$ leading to $k_\infty = 9\times10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(e) Experiments with $M = N_2, O_2$, and synthetic air at pressures from 15–1000 mbar. Falloff extrapolation with $F_c = 0.6$. Effective rate coefficients for HO radical removal in O_2 and synthetic air were markedly lower than in N_2 due to HO radical regeneration by the reaction $C_2H_2OH + O_2 \rightarrow HO + \text{products}$, which shows evidence for an influence of the extent of vibrational deexcitation of C_2H_2OH.

(f) Pressure range 2 mbar–130 bar of He. Falloff curves were constructed with the present and earlier data[3] using a calculated $F_c = \{0.17 \exp(-51/T) + \exp(-T/204)\}$, i.e., $F_c(298\text{ K}) = 0.37$. From a third-law analysis of the equilibrium constant, the value $\Delta H°(0\text{ K}) = -(146\pm10)$ kJ mol^{-1} was derived. The equilibrium constant obtained at temperatures above 700 K is given by $K_c = 5.4\times10^{-2}T^{-1.7}\exp(17560/T)$ bar^{-1}.

(g) Theoretical evaluation of the data of Perry and Williamson[1] and Michael *et al.*,[12] using $F_c = 0.6$ and $k_\infty(300\text{ K}) = 8.3\times10^{-13}$ cm^3 molecule^{-1} s^{-1}. Simulation of k_0 up to a temperature of 1400 K.

(h) Temperature dependence based on data from Refs. 1, 11, and 12 in accord with evaluation from Ref. 7. Absolute value at 298 K based on data from Refs. 3 and 4.

(i) Based on the analysis of Smith *et al.*,[7] which includes data from Refs. 1, 11, 12, and 13.

(j) Based on the data from Refs. 3 and 4 in the falloff range together with the theoretical analysis from Ref. 7.

Preferred Values

$k_0 = 5\times10^{-30}(T/300)^{-1.5}$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–800 K.

Reliability

$\Delta \log k_0 = \pm0.1$ at 298 K.
$\Delta n = \pm1.5$.

Comments on Preferred Values

The preferred rate coefficient at 298 K is based on the experimental data of Schmidt *et al.*,[3] Wahner and Zetzsch,[4] and Bohn *et al.*[5] and the theoretical analysis of Smith *et al.*[7] The temperature dependence is based on the data of Perry *et al.*,[11] Michael *et al.*,[12] and Perry and Williamson[1] as discussed and evaluated by Atkinson.[8] At temperatures above ~500 K another component of the rate coefficient with a much stronger temperature dependence also has to be taken into account.[8] The preferred values should be used in connection with the calculated F_c values from Fulle *et al.*[6] such as given in comment (f) of k_0. Fulle *et al.*[6] provide a set of falloff curves from 250 to 1200 K and from 0.26 to 80 bar which relate the low temperature–low activation energy regime with the high temperature–high activation energy regime. A comparison of earlier data at pressures between 0.01 and 1 bar with the results from Fulle *et al.*[6] at 2 to 80 bar shows considerable inconsistencies. Earlier measurements appeared to level off below 1 bar while Fulle *et al.*[6] find falloff curves leading to k_∞ considerably higher than previous extrapolations. This influences the construction of falloff curves and the extrapolation to k_0.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	References	Technique/Comments
Absolute Rate Coefficients			
$(6.91\pm0.90)\times10^{-13}$	297	Perry and Williamson, 1982[1]	FP-RF (a)
$(8.3\pm0.8)\times10^{-13}$	295	Schmidt *et al.*, 1985[3]	PLP-LIF (b)
9×10^{-13}	298	Wahner and Zetzsch, 1985[4]	PLP-A (c)
$(8.5\pm0.6)\times10^{-13}$	298	Bohn, Siese, and Zetzsch, 1996[5]	PLP-A (d)
$8.5\times10^{-12}\exp(-705/T)$	333–1273	Liu, Mulac, and Jonah, 1988[14]	(e)
8.0×10^{-13}	298*		
$3.8\times10^{-11}\exp(-910/T)$	300–814	Fulle *et al.*, 1997[6]	PLP-LIF (f)
1.8×10^{-12}	298*		
Relative Rate Coefficients			
$(8.4\pm1.4)\times10^{-13}$	298	Atkinson and Aschmann, 1984[15]	RR (g)
$(8.3\pm1.8)\times10^{-13}$	297±2	Hatakeyama, Washida, and Akimoto, 1986[16]	RR (h)
$(7.0\pm0.7)\times10^{-13}$	297±2	Arnts, Seila, and Bufalini, 1989[17]	RR (i)
Reviews and Evaluations			
$9.4\times10^{-12}\exp(-700/T)$	230–500	Atkinson, 1989[8]	(j)
$8.3\times10^{-13}(T/300)^2$	200–300	NASA, 1997[9]	(k)
$9.0\times10^{-13}(T/300)^2$	200–300	IUPAC, 1997[10]	(l)

Comments

(a) See comment (a) for k_0.
(b) See comment (c) for k_0.
(c) See comment (d) for k_0.
(d) See comment (e) for k_0.
(e) Pulse radiolysis technique with resonance absorption measurement of HO radicals. Measurements were conducted at 1 bar of Ar.
(f) See comment (f) for k_0.
(g) HO radicals were generated by the photolysis of CH_3ONO in CH_3ONO–NO–C_2H_2–cyclohexane–air mixtures at 1 bar total pressure. The concentrations of acetylene and cyclohexane were measured by GC. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(HO+\text{cyclohexane})=7.21\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[18]
(h) HO radicals were generated by photolysis of H_2O_2 in air at 254 nm. The concentrations of acetylene and cyclohexane (the reference compound) were monitored by FTIR spectrometry. Measurements were carried out at 1 bar pressure in air. The measured rate coefficient ratio $k(HO+C_2H_2)/k(HO+\text{cyclohexane})=0.116\pm0.025$ is placed on an absolute basis by use of a rate coefficient of $k(HO+\text{cyclohexane})=7.19\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[18]
(i) HO radicals were generated by the photolysis of CH_3ONO in air at 1 bar pressure. The concentrations of acetylene and ethane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(HO+C_2H_2)/k(HO+\text{ethane})=2.84\pm0.26$ (two standard deviations) is placed on an absolute basis by use of a rate coefficient of $k(HO+\text{ethane})=2.46\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).
(j) See comment (h) for k_0.
(k) See comment (i) for k_0.
(l) See comment (j) for k_0.

Preferred Values

No recommendation.

Comments on Preferred Values

The measurements of Fulle *et al.*,[6] carried out at total pressures of He diluent of 2–130 bar, show that the rate coefficient k continues to increase markedly with increasing pressure for pressures above 1 bar. Fulle *et al.*[6] obtained $k_\infty = 3.8\times10^{-11}\exp(-910/T)$ cm^3 molecule^{-1} s^{-1}, with $k_\infty = 1.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and $k=1.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of He, with $F_c=\{0.17\exp(-51/T)+\exp(-T/204)\}$ for M=He ($F_c=0.37$ at 298 K). The results of this study of Fulle *et al.*[6] are, however, inconsistent with several previous absolute rate coefficient studies[1,3–5,11–14] and with the relative rate coefficient studies,[15–17] which indicate a rate coefficient at room temperature and 1 bar of air or N_2 of $(8-9)\times10^{-13}$ cm^3 molecule^{-1} s^{-1}. The relative rate studies of Atkinson and Aschmann,[15] Hatakeyama *et al.*,[16] and Arnts *et al.*,[17] measured the disappearance rate of acetylene in ~1 bar of air; however, the HO radical reaction with acetylene is slow and measurements of this rate coefficient using relative rate methods may be subject to significant uncertainty.

Clearly, relative rate studies[15–17] and absolute rate studies conducted up to ≤1 bar total pressure[1,3–5,11,12,14] lead to a rate coefficient at ~1 bar pressure of air or N_2 markedly lower (by ~40%) than that calculated from the study of Fulle *et al.*,[6] with the earlier absolute studies[1,3–5,11,12,14] also leading to a markedly lower value of k_∞ at room temperature. In view of these inconsistencies, we make no recommendation concerning either the rate coefficient k_∞ or the rate coefficient k at 298 K and 1 bar of air. Further absolute (and relative) rate studies are urgently needed to resolve the above noted discrepancies.

References

[1] R. A. Perry and D. Williamson, Chem. Phys. Lett. **93**, 331 (1982).

[2] W. Hack, K. Hoyermann, R. Sievert, and H. Gg. Wagner, Oxid. Comm. **5**, 101 (1983).

[3] V. Schmidt, G. Y. Zhu, K. H. Becker, and E. H. Fink, Ber. Bunsenges. Phys. Chem. **89**, 321 (1985).

[4] A. Wahner and C. Zetzsch, Ber. Bunsenges. Phys. Chem. **89**, 323 (1985).

[5] B. Bohn, M. Siese, and C. Zetzsch, J. Chem. Soc. Faraday Trans. **92**, 1459 (1996).

[6] D. Fulle, H. F. Hamann, H. Hippler, and C. P. Jänsch, Ber. Bunsenges. Phys. Chem. **101**, 1433 (1997).

[7] G. P. Smith, P. W. Fairchild, and D. R. Crosley, J. Chem. Phys. **81**, 2667 (1984).

[8] R. Atkinson, J. Phys. Ref. Data **Monograph 1**, 1 (1989).

[9] NASA Evaluation No. 12, 1997 (see references in Introduction).

[10] IUPAC, Supplement V, 1997 (see references in Introduction).

[11] R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. **67**, 5577 (1977).

[12] J. V. Michael, D. F. Nava, R. P. Borkowski, W. A. Payne, and L. J. Stief, J. Chem. Phys. **73**, 6108 (1980).

[13] A. V. Pastrana and R. W. Carr, Int. J. Chem. Kinet. **6**, 587 (1974).

[14] A. Liu, W. A. Mulac, and C. D. Jonah, J. Phys. Chem. **92**, 5942 (1988).

[15] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **16**, 259 (1984).

[16] S. Hatakeyama, N. Washida, and H. Akimoto, J. Phys. Chem. **90**, 173 (1986).

[17] R. R. Arnts, R. L. Seila, and J. J. Bufalini, J. Air Pollut. Control Assoc. **39**, 453 (1989).

[18] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$HO + C_2H_4 + M \rightarrow C_2H_4OH + M$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
5.5×10^{-29} [Ar]	296	Zellner and Lorenz, 1984[1]	PLP-RF (a)
$(6.1\pm1.2)\times10^{-29}$ [N_2]	300	Kuo and Lee, 1991[2]	DF-RF (b)
$(5.2\pm1.1)\times10^{-29}$ [O_2]	300		
$4.1\times10^{-29}(T/300)^{-3.4}$ [He]	300–800	Fulle *et al.*, 1997[3]	PLP-LIF (c)
Relative Rate Coefficients			
$(9.5^{+3.2}_{-2.4})\times10^{-29}$ [air]	295	Klein *et al.*, 1984[4]	RR (d)
$(5.9^{+3.0}_{-1.0})\times10^{-29}$ [Ar]	295		
Reviews and Evaluations			
$6\times10^{-29}(T/298)^{-4}$ [air]	295–420	Atkinson, 1994[5]	(e)
$1.0\times10^{-28}(T/300)^{-0.8}$ [air]	200–300	NASA, 1997[6]	(f)
$7\times10^{-29}(T/300)^{-3.1}$ [N_2]	200–300	IUPAC, 1997[7]	(g)

Comments

(a) Pressure range 4–130 mbar; temperature range 296–524 K. Falloff extrapolation using $F_c=0.8$.

(b) Pressure range 0.4–66 mbar. HO radicals were generated by reaction of H atoms with excess NO. Data extrapolated using $F_c=0.7$.

(c) The pressure was varied between 1 mbar and 150 bar. Falloff curves were also constructed using earlier rate data with a calculated $F_c=0.21\exp(-220/T)+\exp(-T/305)$ and $F_c(300)=0.47$. The value $\Delta H°(0\ \text{K})=-(123\pm6)$ kJ mol^{-1} was derived from a third-law analysis of the equilibrium constant K_c for which $K_c=2.1\times10^{-2}T^{-0.95}\exp(14780/T)$ bar^{-1} was obtained from measurements performed at 646–803 K and He pressures up to 140 bar.

(d) HO_2NO_2–NO system used as source of HO radicals. Reaction of HO radicals with C_2H_4 was studied in a 420 L glass reactor relative to HO+n-hexane where the latter reaction was calibrated against absolute measurements of the reaction HO+n-butane [$k(295\ \text{K})=2.53\times10^{-12}$ cm^3 molecule^{-1} s^{-1}]. Pressure range 1.3–1000 mbar, falloff curves constructed with $F_c=0.7$.

(e) Detailed review of all earlier data. The temperature dependence based on the work of Kuo and Lee[2] and a previous evaluation[8] was adopted.

(f) Based on data of Tully,[9] Davis *et al.*,[10] Howard,[11] Greiner,[12] Morris *et al.*,[13] and Overend and Paraskevopoulos[14] in He, Atkinson *et al.*[15] in Ar, and Lloyd *et al.*,[16] Cox,[17] and Klein *et al.*[4] in N_2–O_2 mixtures.

(g) Based on the rate data of Ref. 2 and combined with measurements from Refs. 1 and 3; falloff curves were constructed with $F_c=0.7$.

Preferred Values

$k_0=7\times10^{-29}(T/300)^{-3.1}[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

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

$\Delta n=\pm2$.

Comments on Preferred Values

Because of the smaller scatter of the data from Ref. 1, as well as of the lower data from earlier studies, an average of the available results was preferred with heavier weight given to the smaller values of k_0. Falloff curves are constructed with the calculated $F_c=0.48$ from Ref. 3.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.47\pm0.24)\times10^{-12}$	291	Tully, 1993[9]	PLP-LIF (a)
$3.3\times10^{-12}\exp[(320\pm150)/T]$	296–524	Zellner and Lorenz, 1984[1]	PLP-RF (b)
9.7×10^{-12}	298		
$(9.4\pm1.6)\times10^{-12}$	298	Nielsen *et al.*, 1990[18]	(c)
$(7.7\pm1.0)\times10^{-12}$	298	Becker, Geiger, and Wiessen, 1991[19]	PLP-LIF (d)
1.0×10^{-11}	300–800	Fulle *et al.*, 1997[3]	PLP-LIF (e)
Relative Rate Coefficients			
$(8.11\pm0.37)\times10^{-12}$	299±2	Atkinson *et al.*, 1982[20]	RR (f)
$(8.5\pm0.6)\times10^{-12}$	295	Klein *et al.*, 1984[4]	RR (g)
Reviews and Evaluations			
$9.0\times10^{-12}(T/298)^{-1.1}$	290–525	Atkinson, 1994[5]	(h)
8.8×10^{-12}	200–300	NASA, 1997[6]	(i)
9×10^{-12}	200–300	IUPAC, 1997[7]	(j)

Comments

(a) Higher end of falloff curve at 66–790 mbar; temperature range 291–591 K.

(b) See comment (a) for k_0.

(c) Pulse radiolysis of H_2O–Ar mixtures. HO monitored by UV absorption at 309 nm. Rate coefficient determined at a total pressure of 1 bar.

(d) Experiments were carried out at a total pressure of 1 bar of synthetic air. Numerical simulation with a mechanism of 12 reactions.

(e) See comment (c) for k_0.

(f) HO radicals were generated by photolysis of CH_3ONO in presence of air containing NO. Concentrations of ethene and cyclohexane (the reference compound) were measured by GC. The rate coefficient ratio of $k(\text{HO+ethene})/k(\text{HO+cyclohexane})=1.12\pm0.05$ is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO+cyclohexane}) = 7.24\times10^{-12}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$.[21]

(g) See comment (d) for k_0.

(h) See comment (e) for k_0.

(i) See comment (f) for k_0.

(j) See comment (g) for k_0.

Preferred Values

$k = 7.9\times10^{-12}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K and 1 bar of air.

$k_\infty = 9.0\times10^{-12}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$, independent of temperature over the range 200–300 K.

Reliability

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

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred value is similar to those referred to in Refs. 3, 5, and 19. The recent experiments by Fulle *et al.*[3] confirm temperature independent k_∞ values.[7] Falloff curves should be calculated with the theoretical expression for $F_c = 0.21 \exp(-220/T) + \exp(-T/305)$ which probably applies to M=He as well as N_2.

References

[1] R. Zellner and K. Lorenz, J. Phys. Chem. **88**, 984 (1984).
[2] C.-H. Kuo and Y.-P. Lee, J. Phys. Chem. **95**, 1253 (1991).
[3] D. Fulle, H. F. Hamann, H. Hippler, and C. P. Jänsch, Ber. Bunsenges. Phys. Chem. **101**, 1433 (1997).
[4] Th. Klein, I. Barnes, K. H. Becker, E. H. Fink, and F. Zabel, J. Phys. Chem. **88**, 5020 (1984).
[5] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 2**, 1 (1994).
[6] NASA Evaluation No. 12, 1997 (see references in Introduction).
[7] IUPAC Supplement V, 1997 (see references in Introduction).
[8] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 1**, 1 (1989).
[9] F. P. Tully, Chem. Phys. Lett. **96**, 198 (1983).
[10] D. D. Davis, S. Fischer, R. Schiff, R. T. Watson, and W. Bollinger, J. Chem. Phys. **63**, 1707 (1975).
[11] C. J. Howard, J. Chem. Phys. **65**, 4771 (1976).
[12] N. R. Greiner, J. Chem. Phys. **53**, 1284 (1970).
[13] E. D. Morris, Jr., D. H. Stedman, and H. Niki, J. Am. Chem. Soc. **93**, 3570 (1971).
[14] R. P. Overend and G. Paraskevopoulos, J. Chem. Phys. **67**, 674 (1977).
[15] R. Atkinson, R. A. Perry, and J. N. Pitts, Jr., J. Chem. Phys. **66**, 1197 (1977).
[16] A. C. Lloyd, K. R. Darnall, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **80**, 789 (1976).
[17] R. A. Cox, Int. J. Chem. Kinet. Symp. **1**, 379 (1975).
[18] O. J. Nielsen, O. Jørgensen, M. Donlon, H. W. Sidebottom, D. J. O'Farrell, and J. Treacy, Chem. Phys. Lett. **168**, 319 (1990).
[19] K. H. Becker, H. Geiger, and P. Wiesen, Chem. Phys. Lett. **184**, 256 (1991).
[20] R. Atkinson, S. M. Aschmann, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **14**, 507 (1982).
[21] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$HO + C_2H_6 \rightarrow H_2O + C_2H_5$

$\Delta H^\circ = -76.2\ kJ \cdot mol^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.90 \pm 0.60) \times 10^{-13}$	296	Howard and Evenson, 1976[1]	DF-LMR
$(2.6 \pm 0.4) \times 10^{-13}$	298	Leu, 1979[2]	DF-RF
8.0×10^{-14}	238	Margitan and Watson, 1982[3]	PLP-RF
$1.43 \times 10^{-14}\ T^{1.05} \exp(-911/T)$	297–800	Tully, Ravishankara, and Carr, 1983[4]	FP-RF
$(2.59 \pm 0.21) \times 10^{-13}$	297		
$1.80 \times 10^{-11} \exp[-(1240 \pm 110)/T]$	240–295	Smith *et al.*, 1984[5]	FP-RF
$(2.63 \pm 0.10) \times 10^{-13}$	295		
2.75×10^{-13}	295	Devolder *et al.*, 1984[6]	DF-RF
$(2.67 \pm 0.40) \times 10^{-13}$	295±2	Baulch, Campbell, and Saunders, 1985[7]	DF-RF
$8.51 \times 10^{-18}\ T^{2.06} \exp(-430/T)$	293–705	Tully *et al.*, 1986[8]	PLP-LIF
$(2.39 \pm 0.10) \times 10^{-13}$	292.5		
$(1.27 \pm 0.08) \times 10^{-13}$	248	Stachnik, Molina, and Molina, 1986[9]	PLP-RA
$(1.29 \pm 0.09) \times 10^{-13}$	248		
$(2.51 \pm 0.06) \times 10^{-13}$	297		
$(2.50 \pm 0.06) \times 10^{-13}$	297		
$(2.77 \pm 0.3) \times 10^{-13}$	296±2	Bourmada, Lafage, and Devolder, 1987[10]	DF-RF
$8.4 \times 10^{-12} \exp[-(1050 \pm 100)/T]$	226–363	Wallington, Neuman, and Kurylo, 1987[11]	FP-RF
$(2.30 \pm 0.26) \times 10^{-13}$	296		
$(2.61 \pm 0.13) \times 10^{-13}$	296	Zabarnick, Fleming, and Lin, 1988[12]	PLP-LIF
$(2.38 \pm 0.16) \times 10^{-13}$	297±2	Abbatt, Demerjian, and Anderson, 1990[13]	DF-LIF
$(1.54 \pm 0.24) \times 10^{-11}$	1225	Bott and Cohen, 1991[14]	SH-RA
$1.03 \times 10^{-11} \exp[-(1108 \pm 40)/T]$	231–377	Talukdar *et al.*, 1994[15]	PLP-LIF
$(2.43 \pm 0.13) \times 10^{-13}$	298		
8.37×10^{-12}	970	Koffend and Cohen, 1996[16]	SH-RA
$(2.55 \pm 0.3) \times 10^{-13}$	300	Donahue *et al.*, 1996[17]	DF-LIF
$(2.59 \pm 0.08) \times 10^{-13}$	300	Donahue, Anderson, and Demerjian, 1998[18]	DF-LIF
$(3.55 \pm 0.11) \times 10^{-13}$	325		
$(3.90 \pm 0.12) \times 10^{-13}$	340		
$(4.38 \pm 0.23) \times 10^{-13}$	360		
$(5.61 \pm 0.17) \times 10^{-13}$	375		
$(6.04 \pm 0.18) \times 10^{-13}$	390		
Reviews and Evaluations			
$8.7 \times 10^{-12} \exp(-1070/T)$	220–380	NASA, 1997[19]	(a)
$1.52 \times 10^{-17}\ T^2 \exp(-498/T)$	226–1225	Atkinson, 1997[20]	(b)
$7.9 \times 10^{-12} \exp(-1030/T)$	240–300	IUPAC, 1997[21]	(c)

Comments

(a) The 298 K rate coefficient was derived from the data of Tully *et al.*,[8] Wallington *et al.*,[11] Abbatt *et al.*,[13] Schiffman *et al.*,[22] Talukdar *et al.*,[15] and Anderson and Stephens (unpublished data, 1994), using a temperature dependence of $E/R = 1070$ K to recalculate the reported room temperature data to 298 K. The temperature dependence was derived from the data of Wallington *et al.*,[11] Talukdar *et al.*,[15] and Anderson and Stephens (unpublished data, 1994).

(b) Derived from the absolute rate coefficient data of Howard and Evenson,[1] Leu,[2] Margitan and Watson,[3] Tully *et al.*,[4,8] Smith *et al.*,[5] Devolder *et al.*,[6] Baulch *et al.*,[7] Stachnik *et al.*,[9] Bourmada *et al.*,[10] Wallington *et al.*,[11] Zabarnick *et al.*,[12] Abbatt *et al.*,[13] Bott and Cohen,[14] Talukdar *et al.*,[15] Koffend and Cohen,[16] and Donahue *et al.*[17] These data were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$.

(c) Derived using the absolute rate coefficient data of Howard and Evenson,[1] Leu,[2] Margitan and Watson,[3] Tully *et al.*,[4,8] Smith *et al.*,[5] Devolder *et al.*,[6] Baulch *et al.*,[7] Stachnick *et al.*,[9] Bourmada *et al.*,[10] Wallington *et al.*,[11] Zabarnick *et al.*,[12] Abbatt *et al.*,[13] and Talukdar *et al.*[15] These absolute rate coefficient data were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.52 \times 10^{-17} T^2 \exp(-499/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 226–800 K. The Arrhenius expression, $k = A \exp(-B/T)$, was centered at 265 K and was derived from the three-parameter equation with $A = Ce^2T^2$ and $B = D + 2T$.

Preferred Values

$k = 2.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.8 \times 10^{-12} \exp(-1025/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

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

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

Comments on Preferred Values

The preferred values were obtained by using the absolute rate coefficient data of Howard and Evenson,[1] Leu,[2] Margitan and Watson,[3] Tully *et al.*,[4,8] Smith *et al.*,[5] Devolder *et al.*,[6] Baulch *et al.*,[7] Stachnick *et al.*,[9] Bourmada *et al.*,[10] Wallington *et al.*,[11] Zabarnick *et al.*,[12] Abbatt *et al.*,[13] Bott and Cohen,[14] Talukdar *et al.*,[15] Koffend and Cohen,[16] and Donahue *et al.*[17,18] The absolute rate coefficient data used in the evaluation[1–18] were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.51 \times 10^{-17} T^2 \times \exp(-497/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 226–1225 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three-parameter equation with $A = Ce^2T^2$ and $B = D + 2T$. The room temperature (the temperature not being specified) absolute rate coefficient of Schiffman *et al.*[22] is in good agreement with the preferred 298 K rate coefficient, as are the relative rate coefficients of Baulch *et al.*,[23] Edney *et al.*,[24] and Finlayson-Pitts *et al.*[25]

References

[1] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 4303 (1976).

[2] M.-T. Leu, J. Chem. Phys. **70**, 1662 (1979).

[3] J. J. Margitan and R. T. Watson, J. Phys. Chem. **86**, 3819 (1982).

[4] F. P. Tully, A. R. Ravishankara, and K. Carr, Int. J. Chem. Kinet. **15**, 1111 (1983).

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

[6] P. Devolder, M. Carlier, J. F. Pauwels, and L. R. Sochet, Chem. Phys. Lett. **111**, 94 (1984).

[7] D. L. Baulch, I. M. Campbell, and S. M. Saunders, J. Chem. Soc. Faraday Trans. 1 **81**, 259 (1985).

[8] F. P. Tully, A. T. Droege, M. L. Koszykowski, and C. F. Melius, J. Phys. Chem. **90**, 691 (1986).

[9] R. A. Stachnik, L. T. Molina, and M. J. Molina, J. Phys. Chem. **90**, 2777 (1986).

[10] N. Bourmada, C. Lafage, and P. Devolder, Chem. Phys. Lett. **136**, 209 (1987).

[11] T. J. Wallington, D. M. Neuman, and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 725 (1987).

[12] S. Zabarnick, J. W. Fleming, and M. C. Lin, Int. J. Chem. Kinet. **20**, 117 (1988).

[13] J. P. D. Abbatt, K. L. Demerjian, and J. G. Anderson, J. Phys. Chem. **94**, 4566 (1990).

[14] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **23**, 1017 (1991).

[15] R. K. Talukdar, A. Mellouki, T. Gierczak, S. Barone, S.-Y. Chiang, and A. R. Ravishankara, Int. J. Chem. Kinet. **26**, 973 (1994).

[16] J. B. Koffend and N. Cohen, Int. J. Chem. Kinet. **28**, 79 (1996).

[17] N. M. Donahue, J. S. Clarke, K. L. Demerjian, and J. G. Anderson, J. Phys. Chem. **100**, 5821 (1996).

[18] N. M. Donahue, J. G. Anderson, and K. L. Demerjian, J. Phys. Chem. A **102**, 3121 (1998).

[19] NASA Evaluation No. 12, 1997 (see references in Introduction).

[20] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

[21] IUPAC, Supplement V, 1997 (see references in Introduction).

[22] A. Schiffman, D. D. Nelson, Jr., M. S. Robinson, and D. J. Nesbitt, J. Phys. Chem. **95**, 2629 (1991).

[23] D. L. Baulch, R. J. B. Craven, M. Din, D. D. Drysdale, S. Grant, D. J. Richardson, A. Walker, and G. Watling, J. Chem. Soc. Faraday Trans. 1 **79**, 689 (1983).

[24] E. O. Edney, T. E. Kleindienst, and E. W. Corse, Int. J. Chem. Kinet. **18**, 1355 (1986).

[25] B. J. Finlayson-Pitts, S. K. Hernandez, and H. N. Berko, J. Phys. Chem. **97**, 1172 (1993).

$HO + C_3H_6 + M \rightarrow C_3H_6OH + M$

$\Delta H° = -134$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
8×10^{-28} [Ar]	298	Zellner and Lorenz, 1984[1]	PLP-RF (a)
Relative Rate Coefficients			
8×10^{-27} [Ar] 8×10^{-27} [air]	298	Klein *et al.*, 1984[2]	(b)
Reviews and Evaluations			
$8 \times 10^{-27} (T/300)^{-3.5}$ [N$_2$]	200–300	IUPAC, 1997[3]	(c)

Comments

(a) Pressure range 1.3–170 mbar. Falloff behavior detected, and evaluated with $F_c=0.8$.
(b) HO_2NO_2–NO system used as source of HO radicals. Reaction studied 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 1.3–1000 mbar; falloff effects could be detected. Evaluation with $F_c=0.5$ gives the present k_0 value.
(c) Based on the falloff extrapolations from Refs. 1 and 2. The temperature coefficient of k_0 is estimated by analogy to the reaction $HO+C_2H_4+M\rightarrow C_2H_4OH+M$.

Preferred Values

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

Reliability

$\Delta\log k_0=\pm1.0$ at 298 K.
$\Delta n=\pm1$.

Comments on Preferred Values

The uncertainty of the extrapolated k_0 is large, because th reaction is close to the high-pressure limit at pressures of 1 bar. The preferred values follow the falloff extrapolation from Refs. 1 and 2 which show the smallest scatter. Fallof extrapolations are made using $F_c=0.5$ at 300 K. The temperature coefficient of k_0 is estimated by analogy to the reaction $HO+C_2H_4+M\rightarrow C_2H_4OH+M$. The recommendation of our previous evaluation, IUPAC, 1997[3] are unchanged.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comment
Absolute Rate Coefficients			
$(3.0\pm0.5)\times10^{-11}$	298	Zellner and Lorenz, 1984[1]	PLP-RF (a)
Relative Rate Coefficients			
$(3.0\pm0.2)\times10^{-11}$	295	Klein *et al.*, 1984[2]	(b)
Reviews and Evaluations			
3.0×10^{-11}	200–300	IUPAC, 1997[3]	(c)

Comments

(a) See comment (a) for k_0.
(b) See comment (b) for k_0.
(c) Based on Refs. 1, 2, and 4–7.

Preferred Values

$k=2.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_\infty=3.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta\log k_\infty=\pm0.1$ over the temperature range 200–300 K.
$\Delta n=\pm1$.

Comments on Preferred Values

The preferred values are based on Refs. 1, 2, and 4–7. There is an uncertainty about the extent of falloff at temperatures above 300 K and there is the possibility of a small activation barrier, such as observed in the reactio $HO+C_2H_2+M\rightarrow C_2H_2OH+M$. We here prefer a temperature independent value of k_∞ in contrast to the recommendation of Ref. 8. The recommendations of our previous evaluation, IUPAC, 1997[3] are unchanged.

References

[1] R. Zellner and K. Lorenz, J. Phys. Chem. **88**, 984 (1984).
[2] Th. Klein, I. Barnes, K. H. Becker, E. H. Fink, and F. Zabel, J. Phys Chem. **88**, 5020 (1984).
[3] IUPAC Supplement V, 1997 (see references in Introduction).
[4] CODATA Supplement II, 1984 (see references in Introduction).
[5] IUPAC, Supplement III, 1989 (see references in Introduction).
[6] O. J. Nielsen, O. Jørgensen, M. Donlon, H. W. Sidebottom, D. J O'Farrell, and J. Treacy, Chem. Phys. Lett **168**, 319 (1990).
[7] F. P. Tully and J. E. M. Goldsmith, Chem. Phys. Lett. **116**, 345 (1985).
[8] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 2**, 1 (1994).

$HO + C_3H_8 \rightarrow H_2O + CH_3CH_2\dot{C}H_2$ (1)

$\rightarrow H_2O + CH_3\dot{C}HCH_3$ (2)

$\Delta H^\circ(1) = -79.1$ kJ·mol^{-1}
$\Delta H^\circ(2) = -86.6$ 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			
$1.20\times10^{-11}\exp[-(679\pm38)/T]$	296–497	Greiner, 1970[1]	FP-KS
1.23×10^{-12}	298		
$(2.62\pm0.67)\times10^{-11}$	1220±15	Bott and Cohen, 1984[2]	SH-RA
$(2.19\pm0.60)\times10^{-11}$	1074	Smith *et al.*, 1985[3]	LH-LIF
$(1.20\pm0.18)\times10^{-12}$	295±2	Baulch, Campbell, and Saunders, 1985[4]	DF-RF
$1.04\times10^{-16}\,T^{1.72}\exp(-145/T)$	293–854	Droege and Tully, 1986[5]	PLP-LIF
$(1.10\pm0.04)\times10^{-12}$	293		
$(1.21\pm0.10)\times10^{-12}$	297±2	Abbatt, Demerjian, and Anderson, 1990[6]	DF-LIF
$(1.22\pm0.08)\times10^{-12}$	298	Mac Leod *et al.*, 1990[7]	PLP-LIF
$9.81\times10^{-12}\exp[-(650\pm30)/T]$	233–363	Mellouki *et al.*, 1994[8]	PLP-LIF
$(1.05\pm0.09)\times10^{-12}$	295		
$1.01\times10^{-11}\exp[-(657\pm46)/T]$	233–376	Talukdar *et al.*, 1994[9]	PLP-LIF
$(1.11\pm0.04)\times10^{-12}$	298		
$(1.09\pm0.03)\times10^{-12}$	300	Donahue, Anderson, and Demerjian, 1998[10]	DF-LIF
$(1.37\pm0.04)\times10^{-12}$	325		
$(1.46\pm0.04)\times10^{-12}$	340		
$(1.60\pm0.09)\times10^{-12}$	360		
$(1.85\pm0.06)\times10^{-12}$	375		
$(1.83\pm0.10)\times10^{-12}$	390		
Reviews and Evaluations			
$1.0\times10^{-11}\exp(-660/T)$	230–400	NASA, 1997[11]	(a)
$1.55\times10^{-17}\,T^2\exp(-61/T)$	233–1220	Atkinson, 1997[12]	(b)
$8.0\times10^{-12}\exp(-590/T)$	240–300	IUPAC, 1997[13]	(c)

Comments

(a) The room temperature rate coefficients of Greiner,[1] Bradley *et al.*,[14] Tully *et al.*,[15] Baulch *et al.*,[4] Schmidt *et al.*,[16] Droege and Tully,[5] Abbatt *et al.*,[6] Schiffman *et al.*,[17] Mellouki *et al.*,[8] Talukdar *et al.*,[9] and Anderson and Stephens (unpublished data, 1994) were used to derive the 298 K value. The temperature dependence was derived from a least-squares analysis of the rate coefficients of Droege and Tully[5] at temperatures <400 K, Mellouki *et al.*,[8] Talukdar *et al.*,[9] and Anderson and Stephens (unpublished data, 1994), with the A factor being adjusted to fit the 298 K value.

(b) Derived from the absolute rate coefficient data of Greiner,[1] Bott and Cohen,[2] Smith *et al.*,[3] Baulch *et al.*,[4] Droege and Tully,[5] Abbatt *et al.*,[6] Mac Leod *et al.*,[7] Mellouki *et al.*,[8] and Talukdar *et al.*,[9] and the relative rate coefficients of Baker *et al.*[18,19] and Atkinson *et al.*[20] These data[1–9,18–20] were fitted to the three-parameter equation $k = CT^2\exp(-D/T)$.

(c) Derived from the absolute rate coefficient data of Greiner,[1] Bott and Cohen,[2] Smith *et al.*,[3] Baulch *et al.*,[4] Droege and Tully,[5] Abbatt *et al.*,[6] Mac Leod *et al.*,[7] Mellouki *et al.*,[8] and Talukdar *et al.*,[9] and the relative rate coefficients of Baker *et al.*,[18,19] and Atkinson *et al.*[20] These data[1–9,18–20] were fitted to the three-parameter equation $k = CT^2\exp(-D/T)$, resulting in $k = 1.54\times10^{-17}T^2\exp(-60/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 233–1220 K. The preferred Arrhenius expression, $k = A\exp(-B/T)$, was centered at 265 K, and was derived from the three-parameter equation with $A = Ce^2T^2$ and $B = D + 2T$.

Preferred Values

$k = 1.10\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.0\times10^{-12}\exp(-590/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability
$\Delta\log k = \pm0.08$ at 298 K.
$\Delta(E/R) = \pm150$ K.

Comments on Preferred Values

The absolute rate coefficient data of Greiner,[1] Bott and

Cohen,[2] Smith *et al.*,[3] Baulch *et al.*,[4] Droege and Tully,[5] Abbatt *et al.*,[6] Mac Leod *et al.*,[7] Mellouki *et al.*,[8] Talukdar *et al.*,[9] and Donahue *et al.*[10] were used to derive the preferred value. These data were fitted to the three-parameter equation $k=CT^2 \exp(-D/T)$, resulting in $k=1.54\times10^{-17}T^2 \exp(-61/T)$ cm^3 molecule^{-1} s^{-1} over the range 233–1220 K. The preferred Arrhenius expression, $k=A \exp(-B/T)$, is centered at 265 K, and is derived from the three-parameter equation with $A=Ce^2T^2$ and $B=D+2T$. The relative rate coefficients of Atkinson *et al.*,[20] Baulch *et al.*,[21] Edney *et al.*,[22] Nielsen *et al.*,[23] and Finlayson-Pitts *et al.*[24] are in good agreement with the recommended expression, as is the absolute rate coefficient of Schiffman *et al.*[17] at room temperature (which was not specified). The preferred values are identical to those in our previous evaluation, IUPAC, 1997,[13] although only absolute rate coefficients are now used in the evaluation and a larger data base is used.

Droege and Tully[5] also measured rate coefficients for the reaction of the HO radical with fully and partially deuterated propanes, and derived a value of $k_1/k_2=226\ T^{-0.64}\times\exp(-816/T)$, leading to $k_1=3.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and $k_2=8.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

References

[1] N. R. Greiner, J. Chem. Phys. **53**, 1070 (1970).
[2] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **16**, 1557 (1984).
[3] G. P. Smith, P. W. Fairchild, J. B. Jeffries, and D. R. Crosley, J. Phys. Chem. **89**, 1269 (1985).
[4] D. L. Baulch, I. M. Campbell, and S. M. Saunders, J. Chem. Soc. Faraday Trans. 1 **81**, 259 (1985).
[5] A. T. Droege and F. P. Tully, J. Phys. Chem. **90**, 1949 (1986).
[6] J. P. D. Abbatt, K. L. Demerjian, and J. G. Anderson, J. Phys. Chem. **94**, 4566 (1990).
[7] H. Mac Leod, C. Balestra, J. L. Jourdain, G. Laverdet, and G. Le Bras, Int. J. Chem. Kinet. **22**, 1167 (1990).
[8] A. Mellouki, S. Téton, G. Laverdet, A. Quilgars, and G. Le Bras, J. Chim. Phys. **91**, 473 (1994).
[9] R. K. Talukdar, A. Mellouki, T. Gierczak, S. Barone, S.-Y. Chiang, and A. R. Ravishankara, Int. J. Chem. Kinet. **26**, 973 (1994).
[10] N. M. Donahue, J. G. Anderson, and K. L. Demerjian, J. Phys. Chem. A. **102**, 3121 (1998).
[11] NASA Evaluation No. 12, 1997 (see references in Introduction).
[12] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).
[13] IUPAC, Supplement V, 1997 (see references in Introduction).
[14] J. N. Bradley, W. Hack, K. Hoyermann, and H. Gg. Wagner, J. Chem. Soc. Faraday Trans. 1 **69**, 1889 (1973).
[15] F. P. Tully, A. R. Ravishankara, and K. Carr, Int. J. Chem. Kinet. **15**, 1111 (1983).
[16] V. Schmidt, G. Y. Zhu, K. H. Becker, and E. H. Fink, Ber. Bunsenges Phys. Chem. **89**, 321 (1985).
[17] A. Schiffman, D. D. Nelson, Jr., M. S. Robinson, and D. J. Nesbitt, J. Phys. Chem. **95**, 2629 (1991).
[18] R. R. Baker, R. R. Baldwin, and R. W. Walker, Trans. Faraday Soc. **66**, 2812 (1970).
[19] R. R. Baldwin and R. W. Walker, J. Chem. Soc. Faraday Trans. 1 **75**, 140 (1979).
[20] R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **14**, 781 (1982).
[21] D. L. Baulch, R. J. B. Craven, M. Din, D. D. Drysdale, S. Grant, D. J Richardson, A. Walker, and G. Watling, J. Chem. Soc. Faraday Trans. 1 **79**, 689 (1983).
[22] E. O. Edney, T. E. Kleindienst, and E. W. Corse, Int. J. Chem. Kinet. **18** 1355 (1986).
[23] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Int. J. Chem Kinet. **23**, 1095 (1991).
[24] B. J. Finlayson-Pitts, S. K. Hernandez, and H. N. Berko, J. Phys. Chem **97**, 1172 (1993).

$$\mathrm{HO + CH_3CH_2CH_2CH_3 \rightarrow H_2O + \dot{C}H_2CH_2CH_2CH_3} \quad (1)$$
$$\mathrm{\rightarrow H_2O + CH_3\dot{C}HCH_2CH_3} \quad (2)$$

$\Delta H°(1) = -79.1$ kJ·mol^{-1}
$\Delta H°(2) = -88.0$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.41\times10^{-11}\exp[-(524\pm93)/T]$	298–495	Greiner, 1970[1]	FP-KS
$(2.56\pm0.08)\times10^{-12}$	298		
$(2.35\pm0.35)\times10^{-12}$	298	Stuhl, 1973[2]	FP-RF
$(4.22\pm0.17)\times10^{-12}$	298	Gordon and Mulac, 1975[3]	PR-RA
$(4.15\pm0.17)\times10^{-12}$	381		
$(4.98\pm0.17)\times10^{-12}$	416		
$1.76\times10^{-11}\exp[-(559\pm151)/T]$	298–420	Perry, Atkinson, and Pitts, 1976[4]	FP-RF
$(2.72\pm0.27)\times10^{-12}$	298		
$(2.67\pm0.22)\times10^{-12}$	297±2	Paraskevopoulos and Nip, 1980[5]	FP-RA
$(2.3\pm0.3)\times10^{-12}$	295	Schmidt *et al.*, 1985[6]	PLP-LIF
$2.34\times10^{-17}\,T^{1.95}\exp(134/T)$	294–509	Droege and Tully, 1986[7]	PLP-LIF
$(2.42\pm0.10)\times10^{-12}$	294		
$(2.25\pm0.10)\times10^{-12}$	297±2	Abbatt, Demerjian, and Anderson, 1990[8]	DF-LIF
$(2.32\pm0.08)\times10^{-12}$	~298	Schiffman *et al.*, 1991[9]	PLP-IR
$2.04\times10^{-17}\,T^{2}\exp[(85\pm8)/T]$	231–378	Talukdar *et al.*, 1994[10]	PLP-LIF
$(2.459\pm0.018)\times10^{-12}$	299		
$(2.43\pm0.07)\times10^{-12}$	300	Donahue, Anderson, and Demerjian, 1998[11]	DF-LIF
$(2.74\pm0.08)\times10^{-12}$	325		
$(2.87\pm0.09)\times10^{-12}$	340		
$(3.48\pm0.10)\times10^{-12}$	375		
$(3.54\pm0.11)\times10^{-12}$	390		
Relative Rate Coefficients			
9.9×10^{-12}	753	Baker *et al.*, 1970[12]; Baldwin and Walker, 1979[13]	RR (a)
4.1×10^{-12}	298	Morris and Niki, 1971[14]	DF-MS (b)
$(2.5\pm0.7)\times10^{-12}$	298	Gorse and Volman, 1974[15]	RR (c)
$(9.3\pm0.8)\times10^{-12}$	653	Hucknall, Booth, and Sampson, 1975[16]	RR (d)
$(2.34\pm0.15)\times10^{-12}$	292±2	Campbell, Handy, and Kirby, 1975[17]	RR (e)
$(2.52\pm0.25)\times10^{-12}$	299±2	Atkinson *et al.*, 1981[18]	RR (f)
$(2.71\pm0.32)\times10^{-12}$	295±1	Atkinson and Aschmann, 1984[19]	RR (f)
$(2.70\pm0.34)\times10^{-12}$	300±2	Barnes *et al.*, 1986[20]	RR (g)
$(2.53\pm0.04)\times10^{-12}$	300	Behnke *et al.*, 1988[21]	RR (h)
Reviews and Evaluations			
$1.69\times10^{-17}\,T^{2}\exp(145/T)$	231–753	Atkinson, 1997[22]	(i)

Comments

(a) Derived from the effects of the addition of small amounts of n-butane to slowly reacting mixtures of H_2+O_2. The loss of H_2 was followed by monitoring the pressure change due to the reaction $2H_2+O_2 \rightarrow 2H_2O$, and the loss of n-butane was measured by GC. The rate coefficient ratio $k(\mathrm{HO}+n\text{-butane})/k(\mathrm{HO}+\mathrm{H_2}) = 13.2$ is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO}+\mathrm{H_2}) = 7.51\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 753 K.[23]

(b) The rate coefficient was measured relative to that for the reaction of the HO radical with propene, of $k(\mathrm{HO}+\text{propene}) = 1.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, determined using the same experimental technique.[24]

(c) HO radicals were produced by the photolysis of H_2O_2 at 254 nm, and the formation rate of CO_2 in irradiated H_2O_2–CO-n-butane–O_2 mixtures at a total pressure of 21–29 mbar (16–22 Torr) was measured, leading to a rate coefficient ratio of $k(\mathrm{HO}+n\text{-butane})/k(\mathrm{HO}+\mathrm{CO}) = 19.4\pm4.9$. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO}+\mathrm{CO}) = 1.3\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K (this evaluation).

(d) HO radicals were generated by the decomposition of H_2O_2 in a boric-acid coated reaction, and the concentrations of n-butane and propane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\mathrm{HO}+n\text{-butane})/k(\mathrm{HO}+\text{propane})$

$= 1.54 \pm 0.13$ is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO+propane}) = 6.02 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 653 K.[22]

(e) HO radicals were generated by the dark reaction of H_2O_2 in the presence of NO_2, and the CO_2 formation from the HO+CO reaction was measured by GC. From the variation in CO_2 formation with n-butane/CO concentration ratio, a rate coefficient ratio of $k(\mathrm{HO}+n\text{-butane})/k(\mathrm{HO+CO}) = 14.8 \pm 0.9$ was derived. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO+CO}) = 1.58 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 292 K and a total pressure of ~133 mbar (100 Torr).[25]

(f) HO radicals were generated by the photolysis of CH_3ONO in 1 atm of air. The concentrations of n-butane and propene (the reference organic) were measured by GC. The measured rate coefficient ratios of $k(\mathrm{HO}+n\text{-butane})/k(\mathrm{HO+propene}) = 0.0962 \pm 0.0093$ at (299 ± 2) K[18] and 0.101 ± 0.012 at (295 ± 1) K[19] are placed on an absolute value using a rate coefficient of $k(\mathrm{HO+propene}) = 4.85 \times 10^{-12} \exp(504/T)$ cm^3 molecule^{-1} s^{-1} at atmospheric pressure of air.[22,25]

(g) HO radicals were generated by the photolysis of H_2O_2 in air at atmospheric pressure, and the concentrations of n-butane and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\mathrm{HO}+n\text{-butane})/k(\mathrm{HO+ethene}) = 0.32 \pm 0.04$ is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO+ethene}) = 8.44 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 300 K and atmospheric pressure of air.[22,25]

(h) HO radicals were generated by the photolysis of NO_x–organic–air mixtures at atmospheric pressure. The concentrations of n-butane and n-octane (the reference compound) were measured by GC, and the measured rate coefficient ratio of $k(\mathrm{HO}+n\text{-butane})/k(\mathrm{HO}+n\text{-octane})$ is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO}+n\text{-octane}) = 8.76 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 300 K.[22]

(i) Derived from the absolute rate coefficients of Greiner,[1] Stuhl,[2] Perry *et al.*,[4] Paraskevopoulos and Nip,[5] Droege and Tully,[7] Abbatt *et al.*,[8] and Talukdar *et al.*,[10] and the relative rate coefficient of Baker *et al.*,[12,13] using the expression $k = CT^2 \exp(-D/T)$.

Preferred Values

$k = 2.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.0 \times 10^{-12} \exp(-395/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are based on the absolute rate coefficients of Greiner,[1] Stuhl,[2] Perry *et al.*,[4] Paraskevopoulos and Nip,[5] Droege and Tully,[7] Abbatt *et al.*,[8] Talukdar *et al.*,[10] and Donahue *et al.*[11] The rate coefficients from these studies[1,2,4,5,7,8,10,11] are fitted to the three parameter expression, $k = CT^2 \exp(-D/T)$, resulting in $k = 1.73 \times 10^{-17} T^2 \exp(137/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 231–509 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three-parameter expression with $A = Ce^2T^2$ and $B = D + 2T$.

Droege and Tully[7] also measured rate coefficients for the reaction of the HO radical with n-butane-d_{10}, and derived a value of $k_1/k_2 = 1.035 \exp(-536/T)$, leading to $k_1 = 3.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and $k_2 = 2.06 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

References

[1] N. R. Greiner, J. Chem. Phys. **53**, 1070 (1970).
[2] F. Stuhl, Z. Naturforsch. **28A**, 1383 (1973).
[3] S. Gordon and W. A. Mulac, Int. J. Chem. Kinet. **Symp. 1**, 289 (1975).
[4] R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. **64**, 5314 (1976).
[5] G. Paraskevopoulos and W. S. Nip, Can. J. Chem. **58**, 2146 (1980).
[6] V. Schmidt, G. Y. Zhu, K. H. Becker, and E. H. Fink, Ber. Bunsenges Phys. Chem. **89**, 321 (1985).
[7] A. T. Droege and F. P. Tully, J. Phys. Chem. **90**, 5937 (1986).
[8] J. P. D. Abbatt, K. L. Demerjian, and J. G. Anderson, J. Phys. Chem. **94**, 4566 (1990).
[9] A. Schiffman, D. D. Nelson, Jr., M. S. Robinson, and D. J. Nesbitt, J. Phys. Chem. **95**, 2629 (1991).
[10] R. K. Talukdar, A. Mellouki, T. Gierczak, S. Barone, S.-Y. Chiang, and A. R. Ravishankara, Int. J. Chem. Kinet. **26**, 973 (1994).
[11] N. M. Donahue, J. G. Anderson, and K. L. Demerjian, J. Phys. Chem. A **102**, 3121 (1998).
[12] R. R. Baker, R. R. Baldwin, and R. W. Walker, Trans. Faraday Soc. **66**, 2812 (1970).
[13] R. R. Baldwin and R. W. Walker, J. Chem. Soc. Faraday Trans. 1 **75**, 140 (1979).
[14] E. D. Morris, Jr. and H. Niki, J. Phys. Chem. **75**, 3640 (1971).
[15] R. A. Gorse and D. H. Volman, J. Photochem. **3**, 115 (1974).
[16] D. J. Hucknall, D. Booth, and R. J. Sampson, Int. J. Chem. Kinet. **Symp. 1**, 301 (1975).
[17] I. M. Campbell, B. J. Handy, and R. M. Kirby, J. Chem. Soc. Faraday Trans. 1 **71**, 867 (1975).
[18] R. Atkinson, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Air Pollut. Contr. Assoc. **31**, 1090 (1981).
[19] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **16**, 1175 (1984).
[20] I. Barnes, V. Bastian, K. H. Becker, E. H. Fink, and W. Nelsen, J. Atmos. Chem. **4**, 445 (1986).
[21] W. Behnke, H. Holländer, W. Koch, F. Nolting, and C. Zetzsch, Atmos. Environ. **22**, 1113 (1988).
[22] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).
[23] D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Frank, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, J. Phys. Chem. Ref. Data **21**, 411 (1992).
[24] E. D. Morris, Jr., D. H. Stedman, and H. Niki, J. Am. Chem. Soc. **93**, 3570 (1971).
[25] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 1**, 1 (1989).

$HO + CO \rightarrow H + CO_2$ (1)
$HO + CO + M \rightarrow HOCO + M$ (2)

$\Delta H°(1) = -104.3\ kJ \cdot mol^{-1}$
$\Delta H°(2) = -134\ kJ \cdot mol^{-1}$

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

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_{01} = 1.3 \times 10^{-13}$	298	Forster *et al.*, 1995[1]	PLP-LIF (a)
$k_{02} = 4.1 \times 10^{-33}$ [He]			
$k_{\infty 2} = 9.7 \times 10^{-13}$			
$k_{01} = 1.8 \times 10^{-12} \exp(-2720/T) + 1.6 \times 10^{-13} \exp(-60/T)$	90–3000	Fulle *et al.*, 1996[2]	PLP-LIF (b)
$k_{02} = \{2.0 \times 10^{-32} (T/300)^{-2.7} \times \exp(-490/T)\}$ [He]			
$k_{\infty 2} = 1.8 \times 10^{-11} \exp(-1850/T) + 1.5 \times 10^{-12} \exp(-130/T)$			
Reviews and Evaluations			
1.5×10^{-13} [1+(0.6 P/bar)]	200–300	NASA, 1997[3]	(c)
1.3×10^{-13} [1+(0.6 P/bar) $(300/T)^{1.0}$]	200–300	IUPAC, 1997[4]	(d)

Comments

(a) Pulsed laser photolysis experiments up to 150 bar of the bath gas He. The detection of HO radicals was by saturated LIF. The pressure dependence of k_1 and k_2 were represented by $k_1 = k_{01}\{1 - [x/(x+1)] F_c^{[1+(\log x)^2]^{-1}}\}$ and $k_2 = k_{02}\{(1+y)/(1+x)\} F_c^{[1+(\log x)^2]^{-1}}$, with $x = k_{02}/(k_{\infty 2} - k_{01})$, $y = k_{01}/(k_{\infty 2} - k_{01})$, and $F_c(298\ K) = 0.69$.

(b) Pulsed laser photolysis experiments over the range 80–900 K between 1 and 700 bar of the bath gas He. Detection of HO radicals was by saturated LIF. The data representation was consistent with statistical unimolecular rate theory in the form of comment (a), with $F_c = 0.84$ at 100 K, 0.77 at 200 K, 0.73 at 250 K, and 0.69 at 300 K. Rate data for other bath gases will have to be analyzed by analogy to the He data, leading to different k_{02} and F_c values. The reaction enthalpy for reaction (2) was derived from experiments between 600 and 900 K.

(c) Weighted average of the data of Paraskevopoulos and Irwin,[5] Hofzumahaus and Stuhl,[6] Niki *et al.*,[7] DeMore,[8] and Hynes *et al.*[9] in $M = N_2$ and air at pressures below 1 bar. These experiments all require reanalysis with respect to the partitioning of k into k_1 and k_2 and the respective pressure dependences which, at temperatures near 200 K, are marked at pressures far below 1 bar.

(d) See Comments on Preferred Values.

Preferred Values

$k = 1.3 \times 10^{-13} [1 + (0.6\ P/bar)(300/T)^{1.0}]$ cm³ molecule⁻¹ s⁻¹ over the temperature range 200–300 K and the pressure range ≤1 bar of N_2 or air.

Reliability

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

$\Delta \log k = \pm 0.2$ over the temperature range 200–300 K.

Comments on Preferred Values

The preferred values at 298 K are based on the studies of Forster *et al.*[1] and Fulle *et al.*,[2] and are identical to those in our previous evaluation, IUPAC, 1997.[4] The partitioning of the product channels between reactions (1) and (2) is included on the basis of the studies of Forster *et al.*[1] and Fulle *et al.*[2] Marked changes with decreasing temperature are also accounted for, consistent with the recent experimental data of Fulle *et al.*[2]

References

[1] R. Forster, M. Frost, D. Fulle, H. F. Hamann, H. Hippler, A. Schlepegrell, and J. Troe, J. Chem. Phys. **103**, 2949 (1995).
[2] D. Fulle, H. F. Hamann, H. Hippler, and J. Troe, J. Chem. Phys. **105**, 983 (1996).
[3] NASA Evaluation No. 12, 1997 (see references in Introduction).
[4] IUPAC Supplement V, 1997 (see references in Introduction).
[5] G. Paraskevopoulos and R. S. Irwin, J. Chem. Phys. **80**, 259 (1984).
[6] A. Hofzumahaus and F. Stuhl, Ber. Bunsenges. Phys. Chem. **88**, 557 (1984).
[7] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **88**, 2116 (1984).
[8] W. B. DeMore, Int. J. Chem. Kinet. **16**, 1187 (1984).
[9] A. J. Hynes, P. H. Wine, and A. R. Ravishankara, J. Geophys. Res. **91**, 11815 (1986).

$HO + HCHO \rightarrow H_2O + HCO \quad (1)$
$\rightarrow H + HCOOH \quad (2)$

$\Delta H^\circ = -129.4\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta H^\circ(2) = -91.5\ \mathrm{kJ \cdot mol^{-1}}$

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

$k/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.25\times 10^{-11} \exp[-(88\pm 151)/T]$	299–426	Atkinson and Pitts, 1978[1]	FP-RF
$(9.4\pm 1.0)\times 10^{-12}$	299		
$(1.05\pm 0.11)\times 10^{-11}$	228–362	Stief *et al.*, 1980[2]	FP-RF
$(9.86\pm 1.13)\times 10^{-12}$	298		
$(8.1\pm 1.7)\times 10^{-12}$	296	Temps and Wagner, 1984[3]	DF-LMR
$1.66\times 10^{-11} \exp[-(86\pm 40)/T]$	296–576	Zabarnick, Fleming, and Lin, 1988[4]	PLP-LIF
$(1.25\pm 0.11)\times 10^{-11}$	298±3		
$(7.95^{+2.04}_{1.44})\times 10^{-12}$	298	Yetter *et al.*, 1989[5]	DF-RF
$(1.94\pm 0.30)\times 10^{-11}$	1205±16	Bott and Cohen, 1991[6]	SH-RA
Relative Rate Coefficients			
$(8.40\pm 0.51)\times 10^{-12}$	299±2	Niki *et al.*, 1984[7]	(a)
Reviews and Evaluations			
1.0×10^{-11}	220–580	NASA, 1997[8]	(b)
$8.6\times 10^{-12} \exp(20/T)$	240–300	IUPAC, 1997[9]	(c)

Comments

(a) Relative rate measurement. HO radicals were generated by the photolysis of methyl or ethyl nitrite in air, and the concentration of $^{13}CH_2O$ and ethene (the reference compound) were measured by FTIR absorption spectroscopy during the experiments. The measured rate coefficient ratio of $k(HO+{}^{13}CH_2O)/k(HO+\text{ethene}) = 0.99\pm 0.06$ is placed on an absolute basis by use of a rate coefficient of $k(HO+\text{ethene}) = 8.48\times 10^{-12}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 299 K and atmospheric pressure.[10]

(b) The 298 K rate coefficient was the average of the absolute rate coefficients determined by Atkinson and Pitts,[1] Stief *et al.*,[2] Temps and Wagner,[3] and Zabarnick *et al.*[4] The combined data set yielded no evidence for any temperature dependence of the rate coefficient.

(c) See Comments on Preferred Values.

Preferred Values

$k = 9.2\times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K.

$k = 8.6\times 10^{-12} \exp(20/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ over the temperature range 240–300 K.

$k_1/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 150$ K.
$\Delta(k_1/k) = \pm 0.10$ at 298 K.

Comments on Preferred Values

The absolute rate coefficients of Atkinson and Pitts,[1] Stief *et al.*,[2] Temps and Wagner,[3] Yetter *et al.*,[5] and Bott and Cohen[6] and the relative rate coefficient of Niki *et al.*[7] (for formaldehyde-^{13}C) were fitted to the three parameter expressions $k = CT \exp(-D/T)$ and $k = CT^2 \exp(-D/T)$, resulting in

$$k = 8.24\times 10^{-18} T^2 \exp(753/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

and

$$k = 1.20\times 10^{-14} T \exp(287/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 228–1205 K. The expression $k = CT \exp(-D/T)$ gave a better fit to the data, and the preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter expression with $A = CeT$ and $B = D + T$. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[9]

The product data of Temps and Wagner[3] and Niki *et al.*[7] and the kinetic/modeling results of Yetter *et al.*[5] show that at 298 K this reaction proceeds via pathway (1) to yield H_2O+HCO.

References

[1] R. Atkinson and J. N. Pitts, Jr., J. Chem. Phys. **68**, 3581 (1978).
[2] L. J. Stief, D. F. Nava, W. A. Payne, and J. V. Michael, J. Chem. Phys. **73**, 2254 (1980).
[3] F. Temps and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **88**, 415 (1984).

[4] S. Zabarnick, J. W. Fleming, and M. C. Lin, Int. J. Chem. Kinet. **20**, 117 (1988).
[5] R. A. Yetter, H. Rabitz, F. L. Dryer, R. G. Maki, and R. B. Klemm, J. Chem. Phys. **91**, 4088 (1989).
[6] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **23**, 1075 (1991).
[7] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **88**, 5342 (1984).
[8] NASA Evaluation No. 12, 1997 (see references in Introduction).
[9] IUPAC Supplement V, 1997 (see references in Introduction).
[10] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$HO + CH_3CHO \rightarrow H_2O + CH_3CO$

$\Delta H° = -125.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.53×10^{-11}	298	Morris, Stedman, and Niki, 1971[1]	DF-MS
$6.87\times10^{-12}\exp[(257\pm151)/T]$	299–426	Atkinson and Pitts, 1978[2]	FP-RF
$(1.60\pm0.16)\times10^{-11}$	299		
$7.1\times10^{-12}\exp[(165\pm91)/T]$	253–424	Semmes *et al.*, 1985[3]	FP-RF
$(1.22\pm0.27)\times10^{-11}$	298		
$5.52\times10^{-12}\exp[(307\pm52)/T]$	244–528	Michael, Keil, and Klemm, 1985[4]	DF-RF
$(1.47\pm0.28)\times10^{-11}$	298		
$8.6\times10^{-12}\exp[(200\pm60)/T]$	297–517	Dóbé, Khachatryan, and Bérces, 1989[5]	DF-RF/LIF
$(1.69\pm0.34)\times10^{-11}$	298±2		
$(1.7\pm0.3)\times10^{-11}$	298	Balestra-Garcia, Le Bras, and Mac Leod, 1992[6]	PLP-RF
$(1.44\pm0.25)\times10^{-11}$	298	Tyndall *et al.*, 1995[7]	DF-LIF
$4.31\times10^{-12}\exp[(309\pm19)/T]$	295–550	Taylor *et al.*, 1996[8]	PLP-LIF
1.23×10^{-11}	295		
Relative Rate Coefficients			
$(1.62\pm0.18)\times10^{-11}$	298±2	Niki *et al.*, 1978[9]	(a)
$(1.28\pm0.43)\times10^{-11}$	298±4	Kerr and Sheppard, 1981[10]	(b)
$(1.62\pm0.10)\times10^{-11}$	298±2	Scollard *et al.*, 1993[11]	(c)
Reviews and Evaluations			
$5.6\times10^{-12}\exp(270/T)$	240–530	NASA, 1997[12]	(d)
$5.6\times10^{-12}\exp(310/T)$	240–530	IUPAC, 1997[13]	(e)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of HONO in air, and the concentrations of CH_3CHO and ethene (the reference compound) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(HO+CH_3CHO)/k(HO+\text{ethene}) = 1.9\pm0.2$ is placed on an absolute basis by use of a rate coefficient of $k(HO+\text{ethene}) = 8.52\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure.[14]

(b) Relative rate method. HO radicals were generated by the photolysis of HONO in air, and the concentrations of CH_3CHO and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(HO+CH_3CHO)/k(HO+\text{ethene}) = 1.50\pm0.50$ is placed on an absolute basis by use of a rate coefficient of $k(HO+\text{ethene}) = 8.52\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure.[14]

(c) Relative rate method. HO radicals were generated from the photolysis of CH_3ONO in air, and the concentrations of CH_3CHO and ethene (the reference compound) were measured during the experiments by GC. The measured rate constant ratio is placed on an absolute basis by use of a rate coefficient of $k(HO+\text{ethene}) = 8.52\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure.[14]

(d) The 298 K rate coefficient was based upon the rate coefficient data of Morris *et al.*,[1] Niki *et al.*,[9] Atkinson and Pitts,[2] Kerr and Sheppard,[10] Semmes *et al.*,[3] and Michael *et al.*[4] The temperature dependence was the average of those measured by Atkinson and Pitts,[2] Semmes *et al.*,[3] and Michael *et al.*[4]

(e) See Comments on Preferred Values.

Preferred Values

$k = 1.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.6\times10^{-12}\exp(310/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–530 K.

Reliability.

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

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

Comments on Preferred Values

The preferred values were obtained from a least-squares analysis of the absolute rate coefficient data of Atkinson and Pitts[2] and Michael *et al.*,[4] and the relative rate coefficient of Niki *et al.*[8] at 298 K, and are identical to those in our previous evaluation, IUPAC, 1997.[13] The absolute and relative rate data of Morris *et al.*,[1] Kerr and Sheppard,[10] Balestra-Garcia *et al.*,[6] Scollard *et al.*,[11] and Tyndall *et al.*[7] are in agreement with the preferred 298 K value. The data of Semmes *et al.*,[3] which are lower than the preferred values by up to ~25%, were not used in the evaluation because of their reported difficulties in accurately determining the acetaldehyde concentrations. The absolute rate constants of Taylor *et al.*[8] over the temperature range 295–900 K were not tabulated and only presented graphically; consequently their data have not been used in the evaluation.

While the absolute rate coefficients measured by Dóbé *et al.*[5] for CH_3CHO are in good agreement with the preferred values, their measured rate coefficients for the reactions of the HO radical with the higher aldehydes $(CH_3)_2CHCHO$ and $(CH_3)_3CCHO$ are significantly higher, by factors of ~1.5–2.3, than the rate coefficients of Kerr and Sheppard[10] and Semmes *et al.*[3] (which are in good agreement). Accor ingly, the rate coefficient data of Dóbé *et al.*[5] have not bee used in the evaluation.

References

[1] E. D. Morris, Jr., D. H. Stedman, and H. Niki, J. Am. Chem. Soc. **93**, 35 (1971).

[2] R. Atkinson and J. N. Pitts, Jr., J. Chem. Phys. **68**, 3581 (1978).

[3] D. H. Semmes, A. R. Ravishankara, C. A. Gump-Perkins, and P. H. Win Int. J. Chem. Kinet. **17**, 303 (1985).

[4] J. V. Michael, D. G. Keil, and R. B. Klemm, J. Chem. Phys. **83**, 16 (1985).

[5] S. Dóbé, L. A. Khachatryan, and T. Bérces, Ber. Bunsenges Phys. Che **93**, 847 (1989).

[6] C. Balestra-Garcia, G. Le Bras, and H. Mac Leod, J. Phys. Chem. 9 3312 (1992).

[7] G. S. Tyndall, T. A. Staffelbach, J. J. Orlando, and J. G. Calvert, Int. Chem. Kinet. **27**, 1009 (1995).

[8] P. H. Taylor, M. S. Rahman, M. Arif, B. Dellinger, and P. Marshall, 26 *International Symposium on Combustion, 1996* (The Combustion Ins tute, Pittsburgh, PA, 1996), pp. 497–504.

[9] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phy Chem. **82**, 132 (1978).

[10] J. A. Kerr and D. W. Sheppard, Environ. Sci. Technol. **15**, 960 (1981).

[11] D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, J. Phys. Chem. 9 4683 (1993).

[12] NASA Evaluation No. 12, 1997 (see references in Introduction).

[13] IUPAC Supplement V, 1997 (see references in Introduction).

[14] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$HO + C_2H_5CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.71 \pm 0.24) \times 10^{-11}$	298	Semmes *et al.*, 1985[1]	FP-RF
Relative Rate Coefficients			
$(2.22 \pm 0.09) \times 10^{-11}$	298±2	Niki *et al.*, 1978[2]	(a)
$(1.94 \pm 0.15) \times 10^{-11}$	298±4	Kerr and Sheppard, 1981[3]	(b)
$(1.82 \pm 0.21) \times 10^{-11}$	298	Audley, Baulch, and Campbell, 1981[4]	(c)
$\leq 3.0 \times 10^{-11}$	553	Kaiser. 1983[5]	(d)
$\leq 3.3 \times 10^{-11}$	296	Kerr and Stocker, 1985[6]	(e)
Reviews and Evaluations			
2.0×10^{-11}	298	IUPAC, 1997[7]	(f)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of HONO in air and the concentrations of propanal and ethene (the reference compound) were measured by FTIR absorption spectroscopy during the experiments. The measured rate coefficient ratio of $k(HO+\text{propanal})/k(HO+\text{ethene}) = 2.6 \pm 0.1$ is placed on an absolute basis by use of a rate coefficient of $k(HO+\text{ethene}) = 8.52 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure.[8]

(b) Relative rate method. HO radicals were generated by the photolysis of HONO in air and the concentrations of propanal and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(HO+\text{propanal})/k(HO+\text{ethene}) = 2.28 \pm 0.17$ is placed on an absolute basis by use of a rate coefficient of $k(HO+\text{ethene}) = 8.52 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure.[8]

(c) Relative rate method. HO radicals were generated by the dark reaction of HO_2+NO_2+CO mixtures, and the concentrations of CO_2 measured as a function of the aldehyde concentration for a series of aldehydes. A rate coefficient ratio $k(HO+propanal)/k(HO+CH_3CHO) = 1.14 \pm 0.13$ was derived from experiments carried out with acetaldehyde and propanal, and this ratio is placed on an absolute basis by use of a rate coefficient of $k(HO+CH_3CHO) = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K (this evaluation).

(d) Relative rate method. Oxidation of propanal at 553 K in the presence of O_2 at 67 mbar, with analysis by MS. Relative decay rates of propanal, propene and *trans*-2-butene of $1:0.45 \pm 0.05:1 \pm 0.1$ were measured, and the rate coefficient ratio of $k(HO+propanal)/k(HO + trans\text{-}2\text{-butene}) = 1.0 \pm 0.1$ is placed on an absolute basis by use of a rate coefficient of $k(HO + trans\text{-}2\text{-butene}) = 2.73 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 553 K.[9] Because the HO radical reaction with *trans*-2-butene may be in the fall-off regime at 553 K and 67 mbar (certainly the case for the propene reaction),[9] an upper limit to the rate coefficient is cited.

(e) HO radicals were generated by the photolysis of HONO in air. From measurements of the NO, NO_2, and propanal concentrations in a flowing system (propanal being measured by GC), a rate coefficient ratio of $k(HO+propanal)/k(HO+HONO) \leq 4.0 \pm 1.1$ was derived. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(HO+HONO) = 6.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 296 K.[10]

(f) See Comments on Preferred Values.

Preferred Values

$k = 2.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred rate coefficient is derived from the mean of the absolute rate coefficient of Semmes *et al.*[1] and the relative rate coefficients of Niki *et al.*[2] and Kerr and Sheppard,[3] and is identical to that in our previous evaluation, IUPAC, 1997.[7] The upper limit to the rate coefficient obtained by Kerr and Stocker[6] is consistent with the preferred value. The relative rate coefficient of Audley *et al.*[4] was not used in the evaluation, due to questions concerning the applicability of the experimental technique used.[1,9] The rate coefficient derived by Kaiser[5] at 553 K of $\lesssim 3.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, though of only semiquantitative value, suggests a zero or close to zero temperature dependence, as expected by analogy with HCHO and CH_3CHO. The major reaction channel is expected[9] to be H atom abstraction from the –CHO group to form $H_2O+C_2H_5CO$.

References

[1] D. H. Semmes, A. R. Ravishankara, C. A. Gump-Perkins, and P. H. Wine, Int. J. Chem. Kinet. **17**, 303 (1985).

[2] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **82**, 132 (1978).

[3] J. A. Kerr and D. W. Sheppard, Environ. Sci. Technol. **15**, 960 (1981).

[4] G. J. Audley, D. L. Baulch, and I. M. Campbell, J. Chem. Soc. Faraday Trans. 1 **77**, 2541 (1981).

[5] E. W. Kaiser, Int. J. Chem. Kinet. **15**, 997 (1983).

[6] J. A. Kerr and D. W. Stocker, J. Photochem. **28**, 475 (1985).

[7] IUPAC, Supplement V, 1997 (see references in Introduction).

[8] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

[9] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 1**, 1 (1989).

[10] IUPAC, Supplement VI, 1997 (see references in Introduction).

$HO + CH_3CH_2CH_2CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.7 \times 10^{-12} \exp[(411 \pm 164)/T]$	258–422	Semmes *et al.*, 1985[1]	FP-RF
$(2.06 \pm 0.30) \times 10^{-11}$	298		
Relative Rate Coefficients			
$(2.52 \pm 0.06) \times 10^{-11}$	298±4	Kerr and Sheppard, 1981[2]	(a)
$(2.59 \pm 0.32) \times 10^{-11}$	298	Audley, Baulch, and Campbell, 1981[3]	(b)
Reviews and Evaluations			
$5.26 \times 10^{-12} \exp(446/T)$	258–422	Atkinson, 1989;[4] 1994[5]	(c)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of HONO in air and the concentrations of butanal and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(HO+propanal)/k(HO+ethene) = 2.96 \pm 0.07$ is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO+ethene}) = 8.52\times10^{-12}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K and atmospheric pressure.[4–6]

(b) Relative rate method. HO radicals were generated by the dark reaction of HO_2+NO_2+CO mixtures, and the concentrations of CO_2 measured as a function of the aldehyde concentration for a series of aldehydes. A rate coefficient ratio $k(\mathrm{HO+butanal})/k(\mathrm{HO+CH_3CHO}) = 1.62\pm0.20$ was derived from experiments carried out with acetaldehyde and butanol, and this ratio placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO+CH_3CHO}) = 1.6\times10^{-11}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K (this evaluation).

(c) Based on the absolute and relative rate coefficients of Semmes *et al.*[1] and Kerr and Sheppard.[2]

Preferred Values

$k = 2.3\times10^{-11}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K.

$k = 5.2\times10^{-12}\exp(450/T)$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ over the temperature range 250–430 K.

Reliability

$\Delta \log k = \pm0.15$ at 298 K.

$\Delta \log(E/R) = \pm300$ K.

Comments on Preferred Values

The preferred values are based on a least-squares analysis of the absolute rate coefficients of Semmes *et al.*[1] and the room temperature relative rate constant of Kerr and Sheppard.[2] The relative rate coefficient of Audley *et al.*[3] is in good agreement with the rate coefficients of Semmes *et al.*[1] and Kerr and Sheppard.[2] However, the rate coefficients of Audley *et al.*[3] for 2-methyl-1-propanal, 1-pentanal and 2,2-dimethyl-1-propanal are significantly lower than the values of Semmes *et al.*[1] and Kerr and Sheppard.[2] Accordingly, the rate coefficient of Audley *et al.*[3] for butanal is not used in the evaluation of the preferred values. At room temperature and below, the reaction is expected to proceed primarily by H-atom abstraction from the –CHO group.[4]

References

[1] D. H. Semmes, A. R. Ravishankara, C. A. Gump-Perkins, and P. H. Wine Int. J. Chem. Kinet. **17**, 303 (1985).

[2] J. A. Kerr and D. W. Sheppard, Environ. Sci. Technol. **15**, 960 (1981).

[3] G. J. Audley, D. L. Baulch, and I. M. Campbell, J. Chem. Soc. Faraday Trans. 1 **77**, 2541 (1981).

[4] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 1**, 1 (1989).

[5] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 2**, 1 (1994).

[6] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$HO + (CHO)_2 \rightarrow H_2O + CHOCO$

Rate coefficient data

$k/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.10\pm0.04)\times10^{-11}$	298±2	Plum *et al.*, 1983[1]	(a)
Reviews and Evaluations			
1.1×10^{-11}	298	IUPAC, 1997[2]	(b)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of glyoxal and cyclohexane (the reference compound) were measured by differential optical absorption spectroscopy and GC, respectively. The measured rate coefficient ratio of $k(\mathrm{HO+glyoxal})/k(\mathrm{HO+cyclohexane}) = 1.52\pm0.05$ is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO+cyclohexane}) = 7.21\times10^{-12}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K.[3]

(b) See Comments on Preferred Values.

Preferred Values

$k = 1.1\times10^{-11}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K.

Reliability

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

Comments on Preferred Values

The preferred rate coefficient is based on the study of Plum *et al.*,[1] with increased uncertainty limits, and is identical to that in our previous evaluation, IUPAC, 1997.[2] The rate coefficient at 298 K is similar to those for other aldehydes. A close to zero temperature dependence is expected at around 298 K. The reaction is assumed to proceed via overall H-atom abstraction to yield $H_2O+HC(O)CO$. Niki *et al.*[4] showed from a study of the Cl atom-initiated reaction of glyoxal that at 298 K and 933 mbar (700 Torr) total pressure the HC(O)CO radical reacts by the pathways,

$$HC(O)CO \rightarrow HCO + CO \quad (a)$$

$$HC(O)CO + O_2 \rightarrow HC(O)C(O)OO \quad (b)$$

$$HC(O)CO + O_2 \rightarrow 2CO + HO_2 \quad (c)$$

with $k_b \sim k_c$ and $k_a/k_b = 3.5 \times 10^{18}$ molecule cm^{-3}.

References

[1] C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., Environ. Sci. Technol. **17**, 479 (1983).
[2] IUPAC, Supplement V, 1997 (see references in Introduction).
[3] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).
[4] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **17**, 547 (1985).

$HO + HOCH_2CHO \rightarrow H_2O + HOCH_2CO$ (1)
$\rightarrow H_2O + HOCHCHO$ (2)

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.0 \pm 0.1) \times 10^{-11}$	298±2	Niki *et al.*, 1987[1]	(a)
Branching Ratios			
$k_1/k = 0.80$	298±2	Niki *et al.*, 1987[1]	(b)
$k_2/k = 0.20$	298±2	Niki *et al.*, 1987[1]	(b)
Reviews and Evaluations			
1.0×10^{-11}	298	IUPAC, 1997[2]	(c)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO in air and the concentrations of $HOCH_2CHO$ and acetaldehyde (the reference compound) measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(HO+CH_3CHO)/k(HO+HOCH_2CHO) = 1.6 \pm 0.15$ is placed on an absolute basis by use of a rate constant of $k(HO+CH_3CHO) = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K (this evaluation).

(b) HO radicals were generated by the photolysis of ethyl nitrite in air, and $HOCH_2CHO$ and products [$(CHO)_2$, CO_2, and HCHO] were measured by FTIR absorption spectroscopy. Product formation yields of $(CHO)_2$, 0.211 ± 0.024; CO_2, 0.813 ± 0.032; and HCHO, 0.824 ± 0.046 were obtained, leading to rate coefficient ratios of $k_1/k = 0.80$ and $k_2/k = 0.20$.

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.80$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(k_1/k) = \pm 0.10$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient and branching ratios k_1/k and k_2/k are taken from the study of Niki *et al.*,[1] with the error limits increased accordingly, and are identical to those in our previous evaluation, IUPAC, 1997.[2]

References

[1] H. Niki, P. D. Maker, C. M. Savage, and M. D. Hurley, J. Phys. Chem. **91**, 2174 (1987).
[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$HO + CH_3COCHO \rightarrow H_2O + CH_3COCO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.1\pm1.6)\times10^{-12}$	297	Kleindienst, Harris, and Pitts, 1982[1]	FP-RF
$8.4\times10^{-13}\exp[(830\pm300)/T]$	260–333	Tyndall *et al.*, 1995[2]	DF-LIF
$(1.32\pm0.30)\times10^{-11}$	298		
Relative Rate Coefficients			
$(1.65\pm0.12)\times10^{-11}$	298±2	Plum *et al.*, 1983[3]	(a)
Reviews and Evaluations			
1.5×10^{-11}	298	IUPAC, 1997[4]	(b)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO in air. The concentrations of $CH_3C(O)CHO$ and cyclohexane (the reference compound) were measured by differential optical absorption spectroscopy and GC, respectively. The measured rate coefficient ratio of $k(HO+CH_3C(O)CHO)/k(HO+\text{cyclohexane})=2.29\pm0.16$ is placed on an absolute basis by use of a rate coefficient $k(HO+\text{cyclohexane})=7.21\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.[5]

(b) See Comments on Preferred Values.

Preferred Values

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

Reliability

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

Comments on Preferred Values

The preferred 298 K rate coefficient is an average of the relative rate coefficient of Plum *et al.*[3] and the absolute rate coefficient of Tyndall *et al.*,[2] and is identical to that in our previous evaluation, IUPAC, 1997.[4] The absolute rate coefficient measured by Kleindienst *et al.*[1] may have been low due to the presence of significant levels of low reactivity impurities in the methylglyoxal samples used. The data of Tyndall *et al.*[2] indicate a significant negative temperature dependence; while no recommendation is made concerning the temperature dependence of this reaction a negative temperature dependence is expected at around room temperature (see, for example, the $HO+CH_3CHO$ reaction in this evaluation). The reaction is assumed to proceed via H-atom abstraction to form $H_2O+CH_3C(O)CO$. Green *et al.*[6] have shown that the dominant fate of the $CH_3C(O)CO$ radical under atmospheric conditions is decomposition to form CH_3CO+CO.

References

[1] T. E. Kleindienst, G. W. Harris, and J. N. Pitts, Jr., Environ. Sci. Technol. **16**, 844 (1982).

[2] G. S. Tyndall, T. A. Staffelbach, J. J. Orlando, and J. G. Calvert, Int. J. Chem. Kinet. **27**, 1009 (1995).

[3] C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., Environ. Sci. Technol. **17**, 479 (1983).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

[5] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

[6] M. Green, G. Yarwood, and H. Niki, Int. J. Chem. Kinet. **22**, 689 (1990).

$HO + CH_3COCH_3 \rightarrow H_2O + CH_3COCH_2$

$\Delta H° = -87.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.7\times10^{-12}\exp[-(600\pm75)/T]$	240–440	Wallington and Kurylo, 1987[1]	FP-RF
$(2.16\pm0.16)\times10^{-13}$	296		
$(8.80\pm1.32)\times10^{-12}$	1217	Bott and Cohen, 1991[2]	SH-RA
$(1.25\times10^{-12}\exp[-(561\pm57)/T]$	243–372	Le Calvé *et al.*, 1998[3]	PLP-LIF
$(1.84\pm0.24)\times10^{-13}$	298		
Relative Rate Coefficients			
$(2.7\pm0.1)\times10^{-13}$	303±2	Kerr and Stocker, 1986[4]	(a)
Reviews and Evaluations			
$2.2\times10^{-12}\exp(-685/T)$	240–440	NASA, 1997[5]	(b)
$2.8\times10^{-12}\exp(-760/T)$	240–300	IUPAC, 1997[6]	(c)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of HONO in air, and the concentrations of acetone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO+acetone})/k(\text{HO+ethene}) = 0.032\pm0.001$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO+ethene}) = 8.32\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 303 K and atmospheric pressure.[7]

(b) Based on the rate coefficient studies of Wallington and Kurylo,[1] Kerr and Stocker,[4] Zetzsch (unpublished data, 1982) and Bauerle *et al.* (unpublished data, 1997).

(c) Based on a fit of the data of Wallington and Kurylo,[1] Bott and Cohen,[2] and Kerr and Stocker[4] to the three-parameter expression $k = CT^2\exp(-D/T)$. The cited Arrhenius expression, centered at 265 K, was derived from the three-parameter expression with $A = Ce^2T^2$ and $B = D + 2T$.

Preferred Values

$k = 1.9\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.1\times10^{-12}\exp(-520/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm0.15$ at 298 K.

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

Comments on Preferred Values

The preferred values are based on the absolute rate coefficient data of Wallington and Kurylo[1] and Le Calvé *et al.*[3] These data[1,3] have been fitted to the three-parameter expression $k = CT^2\exp(-D/T)$, resulting in $k = 2.11\times10^{-18}T^2\exp(10/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–440 K. The preferred Arrhenius expression, $k = A\exp(-B/T)$, is centered at 265 K and is derived from the three-parameter equation with $A = Ce^2T^2$ and $B = D + 2T$.

References

[1] T. J. Wallington and M. J. Kurylo, J. Phys. Chem. **91**, 5050 (1987).

[2] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **23**, 1017 (1991).

[3] S. Le Calvé, D. Hitier, G. Le Bras, and A. Mellouki, J. Phys. Chem. A **102**, 4579 (1998).

[4] J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).

[5] NASA Evaluation No. 12, 1997 (see references in Introduction).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

[7] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$HO + CH_3C(O)CH_2CH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.3\times10^{-12}\exp[-(170\pm120)/T]$	240–440	Wallington and Kurylo, 1987[1]	FP-RF
$(1.15\pm0.10)\times10^{-12}$	296		
$1.51\times10^{-12}\exp[-(60\pm61)/T]$	243–372	Le Calvé *et al.*, 1998[2]	PLP-LIF
$(1.19\pm0.18)\times10^{-12}$	298		
Relative Rate Coefficients			
$(3.5\pm1.0)\times10^{-12}$	305±2	Winer *et al.*, 1976[3]	(a)
2.74×10^{-12}	300	Cox, Derwent, and Williams, 1980[4]	(b)
$(9.5\pm0.9)\times10^{-13}$	295±2	Cox, Patrick, and Chant, 1981[5]	(b)
$(9.4\pm1.7)\times10^{-13}$	297	Edney, Kleindienst, and Corse, 1986[6]	(c)
Reviews and Evaluations			
$3.24\times10^{-18}T^2\exp(414/T)$	240–440	Atkinson, 1989;[7] 1994[8]	(d)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of NO_x–organic–air mixtures, and the concentrations of 2-butanone and 2-methylpropene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO+2-butanone)/k(HO+2-methylpropene)$=0.07(\pm30\%)$ is placed on an absolute basis by use of a rate coefficient of k(HO+2-methylpropene)$=4.94\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 305 K.[7–9]

(b) Relative rate method. HO radicals were generated by the photolysis of HONO in air, and the concentrations of 2-butanone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratios k(HO+2-butanone)/k(HO+ethene) are placed on an absolute basis by use of rate coefficients at atmospheric pressure of k(HO+ethene)$=8.44\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 300 K and 8.65×10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K.[7–9]

(c) HO radicals were generated from the photolysis of CH_3ONO in air, and the concentrations of 2-butanone and propane (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO+2-butanone)/k(HO+propane) is placed on an absolute basis by use of a rate coefficient of k(HO+propane)$=1.11\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 297 K (this evaluation).

(d) Based on a least-squares fit of the rate coefficients of Cox *et al.*,[4] Zetzsch *et al.*,[10] Edney *et al.*,[6] and Wallington and Kurylo[1] to the three-parameter expression $k=CT^2\exp(-D/T)$.

Preferred Values

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

$k=1.3\times10^{-12}\exp(-25/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.

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

Comments on Preferred Values

Photolysis of 2-butanone may have contributed to the measured 2-butanone loss rates in the relative rate studies of Winer *et al.*[3] and Cox *et al.*[4] A unit-weighted least-squares analysis of the absolute rate coefficients of Wallington *et al.*[1] and Le Calvé *et al.*,[2] using the three-parameter expression $k=CT^2\exp(-D/T)$, results in $k=2.53\times10^{-18}T^2\exp(503/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–440 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$, is centered at 265 K and is derived from the above three-parameter expression with $A=Ce^2T^2$ and $B=D+2T$.

Cox *et al.*[5] observed acetaldehyde as a product of the HO radical reaction with 2-butanone, with a formation yield of 0.62 ± 0.02. Acetaldehyde is expected to arise from 2-butanone after H-atom abstraction from the $-CH_2-$group, and hence the fraction of the overall HO radical reaction with 2-butanone proceeding via

$$HO+CH_3C(O)CH_2CH_3\rightarrow H_2O+CH_3C(O)\dot{C}HCH_3$$

is ~0.62.

References

[1] T. J. Wallington and M. J. Kurylo, J. Phys. Chem. **91**, 5050 (1987).

[2] S. Le Calvé, D. Hitier, G. Le Bras, and A. Mellouki, J. Phys. Chem. A **102**, 4579 (1998).

[3] A. M. Winer, A. C. Lloyd, K. R. Darnall, and J. N. Pitts, Jr., J. Phys. Chem. **80**, 1635 (1976).

[4] R. A. Cox, R. G. Derwent, and M. R. Williams, Environ. Sci. Technol. **14**, 57 (1980).

[5] R. A. Cox, K. F. Patrick, and S. A. Chant, Environ. Sci. Technol. **15**, 587 (1981).

[6] E. O. Edney, T. E. Kleindienst, and E. W. Corse, Int. J. Chem. Kinet. **18**, 1355 (1986).
[7] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 1**, 1 (1989).
[8] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 2**, 1 (1994).
[9] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).
[10] C. Zetzsch, 7th International Symposium on Gas Kinetics, University of Göttingen, Göttingen, W. Germany, August 23–28, 1982.

$HO + CH_3OH \rightarrow H_2O + CH_2OH$ (1)
$\rightarrow H_2O + CH_3O$ (2)

$\Delta H°(1) = -97.3$ kJ·mol^{-1}
$\Delta H°(2) = -62.3$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.06 \pm 0.10) \times 10^{-12}$	296 ± 2	Overend and Paraskevopoulos, 1978[1]	FP-RA
$(1.00 \pm 0.10) \times 10^{-12}$	298	Ravishankara and Davis, 1978[2]	FP-RF
$4.8 \times 10^{-12} \exp[-(480 \pm 70)/T]$	240–440	Wallington and Kurylo, 1987[3]	FP-RF
$(8.61 \pm 0.47) \times 10^{-13}$	296		
$(1.01 \pm 0.10) \times 10^{-12}$	298 ± 2	McCaulley *et al.*, 1989[4]	DF-LIF
$5.89 \times 10^{-20}\, T^{2.65} \exp(444/T)$	294–865.5	Hess and Tully, 1989[5]	PLP-LIF
$(9.34 \pm 0.41) \times 10^{-13}$	294		
$(9.0 \pm 0.9) \times 10^{-13}$	298 ± 2	Nelson *et al.*, 1990[6]	PR-RA
$(8.64 \pm 1.30) \times 10^{-12}$	1205 ± 16	Bott and Cohen, 1991[7]	SH-RA
Branching Ratios			
$k_2/k = 0.15 \pm 0.08$	298 ± 2	McCaulley *et al.*, 1989[4]	(a)
Reviews and Evaluations			
$6.7 \times 10^{-12} \exp(-600/T)$	240–400	NASA, 1997[8]	(b)
$3.1 \times 10^{-12} \exp(-360/T)$	240–300	IUPAC, 1997[9]	(c)

Comments

(a) Derived from measurements of the rate coefficients for the reactions of the HO radical with CH_3OH, CD_3OH, and CD_3OD and of the DO radical with CH_3OH, CH_3OD, CD_3OH, and CD_3OD, assuming that secondary kinetic isotope effects are negligible.

(b) The 298 K rate coefficient was the average of the absolute rate coefficients of Overend and Paraskevopoulos,[1] Ravishankara and Davis,[2] Hägele *et al.*,[10] Meier *et al.*,[11] Greenhill and O'Grady,[12] Wallington and Kurylo,[3] and Hess and Tully.[5] The temperature dependence was derived from those reported by Greenhill and O'Grady[12] and Wallington and Kurylo.[3]

(c) Derived from the absolute rate coefficients of Overend and Paraskevopoulos,[1] Ravishankara and Davis,[2] Wallington and Kurylo,[3] McCaulley *et al.*,[4] Hess and Tully,[5] Nelson *et al.*,[6] and Bott and Cohen[7] and the relative rate coefficient of Tuazon *et al.*[13] These data[1–7,13] were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 6.01 \times 10^{-18} T^2 \exp(170/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–1205 K. The Arrhenius expression is centered at 265 K and was derived from the three parameter expression with $A = Ce^2T^2$ and $B = D + 2T$.

Preferred Values

$k = 9.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.1 \times 10^{-12} \exp(-360/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

$k_2/k = 0.15$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 200$ K.
$\Delta k_2/k = \pm 0.10$ at 298 K.

Comments on Preferred Values

The preferred rate coefficient is obtained by fitting the absolute rate coefficients of Overend and Paraskevopoulos,[1] Ravishankara and Davis,[2] Wallington and Kurylo,[3] McCaulley *et al.*,[4] Hess and Tully,[5] Nelson *et al.*,[6] and Bott and Cohen[7] to the three parameter expression $k = CT^2 \exp(-D/T)$. This results in $k = 6.01 \times 10^{-18} T^2 \exp(170/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–1205 K. The preferred Arrhenius expression, $k=A\ \exp(-B/T)$, is centered at 265 K, and is derived from the three parameter equation with $A=Ce^2T^2$ and $B=D+2T$. The kinetic[4] and product[10,11] studies show that the reaction proceeds mainly by channel (1) at room temperature, as expected from the thermochemistry of the reaction pathways (1) and (2). The preferred values are identical to those in our previous evaluation, IUPAC, 1997,[9] although only absolute rate coefficients are now used in the evaluation.

References

[1] R. Overend and G. Paraskevopoulos, J. Phys. Chem. **82**, 1329 (1978).

[2] A. R. Ravishankara and D. D. Davis, J. Phys. Chem. **82**, 2852 (1978).

[3] T. J. Wallington and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 1015 (1987).

[4] J. A. McCaulley, N. Kelly, M. F. Golde, and F. Kaufman, J. Phys. Chem. **93**, 1014 (1989).

[5] W. P. Hess and F. P. Tully, J. Phys. Chem. **93**, 1944 (1989).

[6] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

[7] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **23**, 1075 (1991).

[8] NASA Evaluation No. 12, 1997 (see references in Introduction).

[9] IUPAC, Supplement V, 1997 (see references in Introduction).

[10] J. Hägele, K. Lorenz, D. Rhäsa, and R. Zellner, Ber. Bunsenges. Phys. Chem. **87**, 1023 (1983).

[11] U. Meier, H. H. Grotheer, and Th. Just, Chem. Phys. Lett. **106**, 97 (1984).

[12] P. G. Greenhill and B. V. O'Grady, Aust. J. Chem. **39**, 1775 (1986).

[13] E. C. Tuazon, W. P. L. Carter, R. Atkinson, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **15**, 619 (1983).

$$\begin{aligned} \mathrm{HO + C_2H_5OH} &\rightarrow \mathrm{H_2O + CH_2CH_2OH} \quad (1)\\ &\rightarrow \mathrm{H_2O + CH_3CHOH} \quad (2)\\ &\rightarrow \mathrm{H_2O + CH_3CH_2O} \quad (3) \end{aligned}$$

$\Delta H°(1)=-69\ \mathrm{kJ\cdot mol^{-1}}$

$\Delta H°(2)=-109.9\ \mathrm{kJ\cdot mol^{-1}}$

$\Delta H°(3)=-61.8\ \mathrm{kJ\cdot mol^{-1}}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.25\times10^{-11}\exp[-(360\pm52)/T]$	255–459	Greenhill and O'Grady, 1986[1]	FP-RA
$(3.40\pm0.17)\times10^{-12}$	293		
$7.4\times10^{-12}\exp[-(240\pm110)/T]$	240–440	Wallington and Kurylo, 1987[2]	FP-RF
$(3.33\pm0.23)\times10^{-12}$	296		
$(3.26\pm0.14)\times10^{-12}$	293	Hess and Tully, 1988[3]	PLP-LIF (a,b)
$(3.33\pm0.14)\times10^{-12}$	326.5		
$(3.63\pm0.15)\times10^{-12}$	380		
$(3.94\pm0.16)\times10^{-12}$	441		
$(3.32\pm0.16)\times10^{-12}$	295	Hess and Tully, 1988[3]	PLP-LIF (b,c)
$(5.47\pm0.34)\times10^{-12}$	599		
$(3.04\pm0.25)\times10^{-12}$	298±2	Nelson *et al.*, 1990[4]	PR-RA
$k_2+k_3=(8.80\pm1.32)\times10^{-12}$	1204±16	Bott and Cohen, 1991[5]	SH-RA (d)
Relative Rate Coefficients			
$(3.33\pm0.51)\times10^{-12}$	298±2	Nelson *et al.*, 1990[4]	RR (e)
Reviews and Evaluations			
$7.0\times10^{-12}\exp(-235/T)$	240–600	NASA, 1997[6]	(f)
$4.1\times10^{-12}\exp(-70/T)$	270–340	IUPAC, 1997[7]	(g)

Comments

(a) Reaction of $H^{16}O$ radicals.

(b) Thermal decomposition of the $HO^{16}CH_2CH_2$ radical formed by H-atom abstraction from the $-CH_3$ group to regenerate HO^{16} radicals occurs at temperatures >500 K, and hence the HO^{16} rate coefficient data do not yield the rate coefficient $k=(k_1+k_2+k_3)$ above ~500 K. Since thermal decomposition of the $HO^{16}CH_2\dot{C}H_2$ radical does not lead to regeneration of the HO^{18} radical, the HO^{18} rate coefficient data yield the overall reaction rate coefficient, $k=(k_1+k_2+k_3)$.

(c) Rate coefficients for reaction of the HO^{18} radical. HO^{18} radicals generated from pulsed laser photolysis of $H_2{}^{18}O$, with HO^{18} being detected by LIF.

(d) HO radicals were generated by the thermal desorption of *t*-butyl hydroperoxide in a shock tube, with detection by resonance absorption at 309 nm. The measured rate coefficient corresponds to (k_2+k_3) because of the rapid thermal decomposition of the CH_2CH_2OH radical formed in reaction channel (1) (this is the same radical as formed from the addition of HO radicals to ethene).

(e) HO radicals were generated by photolysis of CH_3ONO–NO–air mixtures. The ethanol and cyclohexane (the reference organic) concentrations were measured by GC. The measured rate constant ratio is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO}+\text{cyclohexane})=7.21\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[8]

(f) The 298 K rate coefficient was the average of the room temperature rate coefficients of Campbell *et al.*,[9] Overend and Paraskevopoulos,[10] Ravishankara and Davis,[11] Cox and Goldstone,[12] Kerr and Stocker,[13] Wallington and Kurylo,[2] and Hess and Tully.[3] The temperature dependence was obtained by averaging the temperature dependencies of the rate coefficients reported by Wallington and Kurylo[2] and Hess and Tully.[3]

(g) See Comments on Preferred Values.

Preferred Values

$k=3.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=4.1\times10^{-12}\exp(-70/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.

$k_1/k=0.05$ at 298 K.

$k_3/k=0.05$ at 298 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.

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

$\Delta k_1/k={}^{+0.10}_{-0.05}$ at 298 K.

$\Delta k_3/k={}^{+0.10}_{-0.05}$ at 298 K.

Comments on Preferred Values

The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[7] There is substantial scatter in the room temperature rate coefficients measured to date. The most definite study to date is that of Hess and Tully.[3] The preferred rate coefficient is derived from fitting the HO^{18} and (for temperatures <500 K) the HO^{16} rate coefficient data of Hess and Tully[3] to the three parameter expression $k=CT^2\exp(-D/T)$. This results in $k=6.18\times10^{-18}T^2\times\exp(532/T)$ cm^2 molecule^{-1} s^{-1} over the temperature range 293–599 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$, is centered at 300 K and is derived from this three-parameter expression with $A=Ce^2T^2$ and $B=D+2T$. The rate coefficients calculated from the preferred Arrhenius expression are ~10% higher than the lowest temperature rate coefficients reported by Greenhill and O'Grady[1] (at 255 K) and Wallington and Kurylo[2] (at 240 K). The preferred 298 K rate coefficient is in good agreement with the absolute and relative rate coefficients of Nelson *et al.*[4] The rate coefficient measured by Bott and Cohen[5] at 1204 K, and ascribed to (k_2+k_3), is consistent with the value of $(k_1+k_2+k_3)$ calculated from the recommended three parameter expression and with the rate coefficient k_1 at 1204 K estimated using the procedure of Atkinson.[14]

Meier *et al.*[15] determined that at room temperature the reaction proceeds mainly $(75\%\pm15\%)$ via formation of the $CH_3\dot{C}HOH$ radical, consistent with the expected thermochemistry of the reaction steps. The kinetic data of Hess and Tully[3] for the reactions of the HO^{16} and HO^{18} radicals with ethanol indicate that channel (1) accounts for ~15% of the overall reaction at 600 K, in agreement with the calculated value of ~20% from the estimation procedure of Atkinson.[14] This agreement allows a rate coefficient ratio of $k_1/k=0.05$ at 298 K to be estimated. Assuming that H-atom abstraction from the –OH group in ethanol [channel (3)] has a similar rate coefficient to the analogous channel for methanol (this evaluation) allows $k_3/k=0.05$ at 298 K to be estimated. The resulting value of $k_2/k=0.90$ at 298 K is just consistent with the product data of Meier *et al.*[15]

References

[1] P. G. Greenhill and B. V. O'Grady, Aust. J. Chem. **39**, 1775 (1986).

[2] T. J. Wallington and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 1015 (1987).

[3] W. P. Hess and F. P. Tully, Chem. Phys. Lett. **152**, 183 (1988).

[4] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

[5] J. F. Bott and N. Cohen, Int. J. Chem. Kinet. **23**, 1075 (1991).

[6] NASA Evaluation No. 12, 1997 (see references in Introduction).

[7] IUPAC, Supplement V, 1997 (see references in Introduction).

[8] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

[9] I. M. Campbell, D. F. McLaughlin, and B. J. Handy, Chem. Phys. Lett. **38**, 362 (1976).

[10] R. Overend and G. Paraskevopoulos, J. Phys. Chem. **82**, 1329 (1978).

[11] A. R. Ravishankara and D. D. Davis, J. Phys. Chem. **82**, 2852 (1978).

[12] R. A. Cox and A. Goldstone, *Proceedings of the 2nd European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants* (D. Reidel, Dordrecht, Holland, 1982), pp. 112–119.

[13] J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).

[14] R. Atkinson, Int. J. Chem. Kinet. **19**, 799 (1987).

[15] U. Meier, H. H. Grotheer, G. Riekert, and Th. Just, Chem. Phys. Lett. **115**, 221 (1985).

HO + $CH_3CH_2CH_2OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.33\pm0.54)\times10^{-12}$	296±2	Overend and Paraskevopoulos, 1978[1]	FP-RA
$(5.34\pm0.39)\times10^{-12}$	296	Wallington and Kurylo, 1987[2]	FP-RF
$(5.64\pm0.48)\times10^{-12}$	298±2	Nelson *et al.*, 1990[3]	PR-RA
Relative Rate Coefficients			
$(3.9\pm0.7)\times10^{-12}$	292	Campbell, McLaughlin, and Handy, 1976[4]	(a)
$(5.29\pm0.43)\times10^{-12}$	298±2	Nelson *et al.*, 1990[3]	(b)
Reviews and Evaluations			
5.5×10^{-12}	298	IUPAC, 1997[5]	(c)

Comments

(a) Relative rate method. HO radicals were generated by the dark reaction of H_2O_2–NO_2 mixtures in the presence of CO and an organic compound. From experiments using n-butane and 1-propanol, a rate coefficient ratio of $k(\mathrm{HO}+1\text{-propanol})/k(\mathrm{HO}+n\text{-butane})=1.67\pm0.27$ (two standard deviations) was derived. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO}+n\text{-butane})=2.36\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 292 K (this evaluation).

(b) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 1-propanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio $k(\mathrm{HO}+1\text{-propanol})/k(\mathrm{HO}+\text{cyclohexane})$ is placed on an absolute basis by use of a rate coefficient $k(\mathrm{HO}+\text{cyclohexane})=7.21\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.[6]

(c) See Comments on Preferred Values.

Preferred Values

$k=5.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The experimental technique of Campbell *et al.*[4] was possibly prone to unrecognized problems,[7] and hence this rate coefficient was not used in deriving the preferred values. The 298 K value is the mean of the absolute rate coefficients of Overend and Paraskevopoulos,[1] Wallington and Kurylo,[2] and Nelson *et al.*[3] and the relative rate coefficient of Nelson *et al.*[3] The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[5]

References

[1] R. Overend and G. Paraskevopoulos, J. Phys. Chem. **82**, 1329 (1976).

[2] T. J. Wallington and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 1015 (1987).

[3] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

[4] I. M. Campbell, D. F. McLaughlin, and B. J. Handy, Chem. Phys. Lett. **38**, 362 (1976).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

[6] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

[7] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 1**, 1 (1989).

$$\begin{aligned} HO + CH_3CH(OH)CH_3 &\rightarrow H_2O + (CH_3)_2CHO & (1)\\ &\rightarrow H_2O + CH_3C(OH)CH_3 & (2)\\ &\rightarrow H_2O + CH_3CH(OH)CH_2 & (3)\end{aligned}$$

$\Delta H°(1) = -60.9$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.48 \pm 0.55) \times 10^{-12}$	296±2	Overend and Paraskevopoulos, 1978[1]	FP-RA
$5.8 \times 10^{-12} \exp[-(30 \pm 90)/T]$	240–440	Wallington and Kurylo, 1987[2]	FP-RF
$(5.81 \pm 0.34) \times 10^{-12}$	296		
$(5.69 \pm 1.09) \times 10^{-12}$	298±2	Nelson *et al.*, 1990[3]	PR-RA
$1.044 \times 10^{-17}\, T^{1.86} \exp(736/T)$	293–587	Dunlop and Tully, 1993[4]	PLP-LIF (a)
$(5.10 \pm 0.21) \times 10^{-12}$	293		
Relative Rate Coefficients			
$(5.56 \pm 0.72) \times 10^{-12}$	298±2	Nelson *et al.*, 1990[3]	(b)
Reviews and Evaluations			
$4.06 \times 10^{-18}\, T^2 \exp(788/T)$	293–587	Atkinson, 1994[5]	(c)
$2.7 \times 10^{-12} \exp(190/T)$	270–340	IUPAC, 1997[6]	(d)

Comments

(a) The reactions of HO^{16} radicals were studied over the temperature range 293–745 K and the reactions of HO^{18} radicals were studied at 548 and 587 K. Nonexponential decays of HO^{16} radicals were observed over the temperature range 504–600 K and, while exponential HO^{16} radical decays were observed above 600 K, the rate coefficients were significantly lower than expected from extrapolation of the lower temperature data. These observations are consistent with thermal decomposition of the $CH_3CH(OH)CH_2$ radical formed in reaction channel (3) [the same radical as formed from HO radical addition to propene] at temperatures $\gtrsim$500 K. Hence using HO^{16} radicals, values of $(k_1 + k_2 + k_3)$ were measured at temperatures $\leqslant$500 K and $(k_1 + k_2)$ at temperatures $\gtrsim$600 K. No regeneration of HO^{18} radicals from thermal decomposition of the $CH_3CH(^{16}OH)CH_2$ radical can occur, and hence the measured HO^{18} rate coefficients are those for $(k_1 + k_2 + k_3)$.

(b) Relative rate measurement. HO radicals were generated by the photolysis of CH_3ONO in air. The concentrations of 2-propanol and cyclohexane (the reference organic) were measured by GC. The measured rate coefficient ratio k(HO+2-propanol)/k(HO+cyclohexane) is placed on an absolute basis by use of a rate coefficient of k(HO+cyclohexane)$= 7.21 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.[7]

(c) Derived from the HO^{18} radical and (for temperatures $\leqslant$502 K) HO^{16} radical rate coefficients of Dunlop and Tully.[4] These rate coefficients[4] were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$.

(d) See Comments on Preferred Values.

Preferred Values

$k = 5.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.7 \times 10^{-12} \exp(190/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.

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

Comments on Preferred Values

The preferred rate coefficients are derived from the data obtained by Dunlop and Tully.[4] The HO^{18} rate coefficients at 548 and 587 K and the HO^{16} rate coefficients at $\leqslant$502 K were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 4.06 \times 10^{-18} T^2 \times \exp(788/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 293–587 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three parameter expression with $A = Ce^2T^2$ and $B = D + 2T$. The preferred rate coefficients are ~10% lower than those of Wallington and Kurylo[2] over the temperature range 270–340 K, and are in agreement within the cited error limits with the room temperature absolute and relative rate coefficients of Overend and Paraskevopoulos[1] and Nelson *et al.*[3] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[6]

References

[1]R. Overend and G. Paraskevopoulos, J. Phys. Chem. **82**, 1329 (1978).
[2]T. J. Wallington and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 1015 (1987).
[3]L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).
[4]J. R. Dunlop and F. P. Tully, J. Phys. Chem. **97**, 6457 (1993).
[5]R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 2**, 1 (1994).
[6]IUPAC, Supplement V, 1997 (*see references in Introduction*).
[7]R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

HO + $CH_3CH_2CH_2CH_2OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.31\pm0.63)\times10^{-12}$	296	Wallington and Kurylo, 1987[1]	FP-RF
$(7.80\pm0.20)\times10^{-12}$	298±2	Nelson *et al.*, 1990[2]	PR-RA
$(9.60\pm0.41)\times10^{-12}$	293	Tully, 1990[3]	PLP-LIF
Relative Rate Coefficients			
$(7.1\pm1.4)\times10^{-12}$	292	Campbell, McLaughlin, and Handy, 1976[4]	(a)
$(8.24\pm0.68)\times10^{-12}$	298±2	Nelson *et al.*, 1990[2]	(b)
Reviews and Evaluations			
8.57×10^{-12}	298	Atkinson, 1994[5]	(c)

Comments

(a) Relative rate method. HO radicals were generated by the dark reaction of H_2O_2–NO_2 mixtures in the presence of CO and an organic compound. From experiments using n-butane and 1-butanol, a rate coefficient ratio of $k(\mathrm{HO}+1\text{-butanol})/k(\mathrm{HO}+n\text{-butane}) = 3.00 \pm 0.56$ (two standard deviations) was derived. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO}+n\text{-butane}) = 2.36\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 292 K (this evaluation).

(b) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 1-butanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio $k(\mathrm{HO}+1\text{-butanol})/k(\mathrm{HO}+\text{cyclohexane})$ is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO}+\text{cyclohexane}) = 7.21\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.[6]

(c) Based on the absolute rate coefficients of Wallington and Kurylo,[1] Nelson *et al.*,[2] and Tully[3] and the relative rate coefficient of Nelson *et al.*[2]

Preferred Values

$k = 8.1\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The experimental technique of Campbell *et al.*[4] was possibly prone to unrecognized problems,[5] and hence this rate coefficient was not used in deriving the preferred value. The preferred value is the average of the absolute rate coefficients of Wallington and Kurylo[1] and Nelson *et al.*[2] and the relative rate coefficient of Nelson *et al.*[2] The unpublished absolute rate coefficient of Tully[3] is ~20% higher than this recommendation.

References

[1]T. J. Wallington and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 1015 (1987).
[2]L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).
[3]F. P. Tully (unpublished data cited in Ref. 2).
[4]I. M. Campbell, D. F. McLaughlin, and B. J. Handy, Chem. Phys. Lett. **38**, 362 (1976).
[5]R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 2**, 1 (1994).
[6]R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$HO + CH_3CH(OH)CH_2CH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(8.89 \pm 0.51) \times 10^{-12}$	296 ± 2	Chew and Atkinson, 1996[1]	(a)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 2-butanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(HO + 2\text{-butanol})/k(HO + \text{cyclohexane}) = 1.24 \pm 0.07$ is placed on an absolute basis by use of a rate coefficient of $k(HO + \text{cyclohexane}) = 7.17 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 296 K.[2]

Preferred Values

$k = 8.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is based on the sole study of Chew and Atkinson,[1] with expanded error limits.

References

[1] A. A. Chew and R. Atkinson, J. Geophys. Res. **101**, 28649 (1996).
[2] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$HO + CH_3OCH_3 \rightarrow H_2O + CH_3OCH_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.29 \times 10^{-11} \exp[-(388 \pm 151)/T]$	299–424	Perry, Atkinson, and Pitts, 1977[1]	FP-RF
$(3.50 \pm 0.35) \times 10^{-12}$	299		
$1.04 \times 10^{-11} \exp[-(372 \pm 34)/T]$	295–442	Tully and Droege, 1987[2]	PLP-LIF
$(2.95 \pm 0.12) \times 10^{-12}$	295		
$6.7 \times 10^{-12} \exp[-(300 \pm 70)/T]$	240–440	Wallington *et al.*, 1988[3]	FP-RF
$(2.49 \pm 0.22) \times 10^{-12}$	296		
$(2.35 \pm 0.24) \times 10^{-12}$	298 ± 2	Nelson *et al.*, 1990[4]	PR-RA
$6.38 \times 10^{-12} \exp[-(234 \pm 34)/T]$	230–372	Mellouki, Teton, and Le Bras, 1995[5]	PLP-LIF
$(2.82 \pm 0.21) \times 10^{-12}$	295		
$3.39 \times 10^{-24} T^{4.11} \exp[(1221 \pm 252)/T]$	295–650	Arif, Taylor, and Dellinger, 1997[6]	PLP-LIF
$(2.95 \pm 0.21) \times 10^{-12}$	295		
Relative Rate Coefficients			
$(2.20 \pm 0.22) \times 10^{-12}$	295 ± 3	Wallington *et al.*, 1989[7]	RR (a)
$(3.07 \pm 0.68) \times 10^{-12}$	298 ± 2	Nelson *et al.*, 1990[4]	RR (b)
Reviews and Evaluations			
$1.0 \times 10^{-11} \exp(-370/T)$	290–450	IUPAC, 1997[8]	(c)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. The concentrations of dimethyl ether and n-butane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(CH_3OCH_3)/k(n\text{-butane}) = 0.918 \pm 0.090$ is placed on an absolute basis by using a rate coefficient of $k(n\text{-butane}) = 2.40 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) HO radicals were generated by the photolysis of

CH_3ONO–NO–air mixtures at atmospheric pressure. The concentrations of dimethyl ether and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio $k(CH_3OCH_3)/k$(cyclohexane) is placed on an absolute basis by use of a rate coefficient of $k(\text{cyclohexane})=7.21\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.[9]

(c) Based on the absolute rate coefficient data of Tully and Droege.[2]

Preferred Values

$k=2.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=5.9\times10^{-12}\exp(-220/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

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

$\Delta(E/R)=\pm150$ K.

Comments on Preferred Values

The reported room temperature absolute[1–6] and relative[4,7] rate coefficients exhibit appreciable scatter, covering a range of a factor of 1.6. The measured temperature dependencies[1–3,5,6] are in reasonable agreement. The preferred values are based on the absolute rate coefficient studies of Tully and Droege,[2] Mellouki *et al.*,[5] and Arif *et al.*,[6] the data of which are between those of the other two absolute temperature-dependent studies of Perry *et al.*[1] and Wallington *et al.*[3]

Because Arrhenius plots of the data of Mellouki *et al.*[5] and Arif *et al.*[6] show curvature, the rate coefficients of Tully and Droege,[2] Mellouki *et al.*,[5] and Arif *et al.*[6] have been fitted to the expression $k=CT^2\exp(-D/T)$, resulting in $k=1.13\times10^{-17}T^2\exp(310/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–650 K. The preferred Arrhenius expression $k=A\exp(-B/T)$ is centered at 265 K and is derived from the three-parameter expression with $A=Ce^2T^2$ and $B=D+2T$.

References

[1] R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. **67**, 611 (1977).
[2] F. P. Tully and A. T. Droege, Int. J. Chem. Kinet. **19**, 251 (1987).
[3] T. J. Wallington, R. Liu, P. Dagaut, and M. J. Kurylo, Int. J. Chem. Kinet. **20**, 41 (1988).
[4] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).
[5] A. Mellouki, S. Teton, and G. Le Bras, Int. J. Chem. Kinet. **27**, 791 (1995).
[6] M. Arif, B. Dellinger, and P. H. Taylor, J. Phys. Chem. A **101**, 2436 (1997).
[7] T. J. Wallington, J. M. Andino, L. M. Skewes, W. O. Siegl, and S. M. Japar, Int. J. Chem. Kinet. **21**, 993 (1989).
[8] IUPAC, Supplement V, 1997 (see references in Introduction).
[9] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$HO + CH_3COCH_2OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.0\pm0.3)\times10^{-12}$	298	Dagaut *et al.*, 1989[1]	FP-RF
Reviews and Evaluations			
3.0×10^{-12}	298	IUPAC, 1997[2]	(a)

Comments

(a) See Comments on Preferred Values.

Preferred Values

$k=3.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is based on the sole study of Dagaut *et al.*,[1] with expanded uncertainty limits, and is identical to that in our previous evaluation, IUPAC, 1997.[2]

References

[1] P. Dagaut, R. Liu, T. J. Wallington, and M. J. Kurylo, J. Phys. Chem. **93**, 7838 (1989).
[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$$\mathrm{HO + CH_3OOH \rightarrow H_2O + CH_2OOH} \quad (1)$$
$$\mathrm{\rightarrow H_2O + CH_3OO} \quad (2)$$

$\Delta H^\circ(2) = -140\ \mathrm{kJ \cdot mol^{-1}}$

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

$k/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.93 \times 10^{-12} \exp[(190 \pm 14)/T]$	223–423	Vaghjiani and Ravishankara, 1989[1]	(a)
5.54×10^{-12}	298		
$k_2 = 1.78 \times 10^{-12} \exp[(220 \pm 21)/T]$	203–348	Vaghjiania and Ravishankara, 1989[1]	(a)
$k_2 = (3.85 \pm 0.23) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(1.02 \pm 0.08) \times 10^{-11}$	~298	Niki *et al.*, 1983[2]	RR (b)
$(1.09 \pm 0.12) \times 10^{-11}$	~298	Niki *et al.*, 1983[2]	RR (c)
Reviews and Evaluations			
$3.8 \times 10^{-12} \exp(200/T)$	200–430	NASA, 1997[3]	(d)
$2.9 \times 10^{-12} \exp(190/T)$	220–430	IUPAC, 1997[4]	(e)

Comments

(a) $\mathrm{HO^{16}}$, $\mathrm{HO^{18}}$, and DO radicals were generated by flash photolysis or pulsed laser photolysis of the following precursors: for $\mathrm{HO^{16}}$; $\mathrm{CH_3OOH}$, $\mathrm{H_2O^{16}}$, and $\mathrm{O_3–H_2O^{16}}$; for $\mathrm{HO^{18}}$; $\mathrm{H_2O^{18}}$, and $\mathrm{O_3–H_2O^{18}}$; and for DO; $\mathrm{D_2O}$, $\mathrm{O_3–D_2O}$, and $\mathrm{O_3–D_2}$, and were monitored by LIF. Rate coefficients $(k_1 + k_2)$ were obtained from measurements of the decay rates of $\mathrm{HO^{18}}$ and DO radicals in the presence of excess $\mathrm{CH_3OOH}$. Rate coefficients k_2 were obtained from the decay rates of $\mathrm{HO^{16}}$ radicals in the presence of $\mathrm{CH_3OOH}$. The $\mathrm{CH_2OOH}$ radical formed in reaction channel (1) rapidly decomposes to HO+HCHO, and hence the use of $\mathrm{HO^{16}}$ allowed only the rate coefficient k_2 to be measured.

(b) HO radicals were generated by the photolysis of $\mathrm{CH_3ONO}$ or $\mathrm{C_2H_5ONO}$ in air. The concentrations of $\mathrm{CH_3OOH}$ and ethene (the reference organic) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\mathrm{HO+CH_3OOH})/k(\mathrm{HO+ethene}) = 1.20 \pm 0.09$ is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO+ethene}) = 8.52 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K and atmospheric pressure of air.[5,6]

(c) HO radicals were generated by the photolysis of $\mathrm{CH_3ONO}$ in air and the concentrations of $\mathrm{CH_3OOH}$ and $\mathrm{CH_3CHO}$ (the reference organic) measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\mathrm{HO+CH_3OOH})/k(\mathrm{HO+CH_3CHO}) = 0.68 \pm 0.07$ is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO+CH_3CHO}) = 1.6 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K (this evaluation).

(d) The 298 K rate coefficient was the average of those of Niki *et al.*[2] and Vaghjiani and Ravishankara.[1] The temperature dependence was that measured by Vaghjiani and Ravishankara.[1]

(e) See Comments on Preferred Values.

Preferred Values

$k = 5.5 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K.

$k = 2.9 \times 10^{-12} \exp(190/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ over the temperature range 220–430 K.

$k_1/k = 0.35$ over the temperature range 220–430 K.

Reliability

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

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

$\Delta(k_1/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred values are those of Vaghjiani and Ravishankara.[1] The preferred branching ratio, also taken from the absolute rate coefficient study of Vaghjiani and Ravishankara,[1] is in good agreement with the earlier measurement of Niki *et al.*[2] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

References

[1] G. L. Vaghjiani and A. R. Ravishankara, J. Phys. Chem. **93**, 1948 (1989).
[2] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **87**, 2190 (1983).
[3] NASA Evaluation No. 12, 1997 (see references in Introduction).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).
[5] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 1**, 1 (1989).
[6] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

HO + HCOOH → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.62\pm0.78)\times10^{-13}$	298–430	Wine, Astalos, and Mauldin, 1985[1]	FP/PLP-RF (a)
$(4.90\pm0.12)\times10^{-13}$	296	Jolly *et al.*, 1986[2]	PLP-RA (b)
$2.91\times10^{-13}\exp[(102\pm194)/T]$	297–445	Singleton *et al.*, 1988[3]	PLP-RA
$(4.47\pm0.28)\times10^{-13}$	297		
$(3.7\pm0.4)\times10^{-13}$	298	Dagaut *et al.*, 1988[4]	FP-RF
Reviews and Evaluations			
4.0×10^{-13}	290–450	NASA, 1997[5]	(c)
4.5×10^{-13}	290–450	IUPAC, 1997[6]	(d)

Comments

(a) H atom formation was also measured by resonance fluorescence, and an H-atom formation yield of 0.75 ±0.25 measured. At 298 K, the measured rate coefficient for the reaction of the HO radical with DC(O)OH was identical to that for HO radical reaction with HC(O)OH.

(b) Experiments with added O_2 led to nonexponential and slower HO radical decays, indicating the formation of H atoms from the HO radical reaction with HC(O)OH.

(c) Based on the data of Zetzsch and Stuhl,[7] Wine *et al.*,[1] Jolly *et al.*,[2] Singleton *et al.*,[3] and Dagaut *et al.*[4]

(d) See Comments on Preferred Values.

Preferred Values

$k=4.5\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–450 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.

$\Delta(E/R)=\pm250$ K.

Comments on Preferred Values

A major problem with the determination of the rate coefficient for this reaction concerns the ready dimerization of HC(O)OH. The studies of Wine *et al.*,[1] Jolly *et al.*,[2] and Singleton *et al.*[3] monitored formic acid in the experimental systems used by UV absorption spectroscopy. The data from these studies[1-3] agree well, and are in reasonable agreement with the room temperature rate coefficient of Dagaut *et al.*[4] The data of Wine *et al.*[1] and Singleton *et al.*[3] show that the temperature dependence of the rate coefficient is zero within the experimental uncertainties. The average of the rate coefficient data of Wine *et al.*,[1] Jolly *et al.*,[2] and Singleton *et al.*[3] has been used to derive the preferred rate coefficient. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[6]

The studies of Wine *et al.*[1] and Jolly *et al.*[2] showed that H atoms are produced in this reaction, with a yield of 0.75 ±0.25.[1] Furthermore, Wine *et al.*[1] and Singleton *et al.*[3] showed that within the experimental uncertainties the rate coefficient for the reaction of the HO radical with DC(O)OH is identical to that for HC(O)OH at 298 K. Also, the room temperature rate coefficients for the reactions of the DO radical with HC(O)OD and DC(O)OD are significantly lower than those for the reactions of the HO radical with HC(O)OH and DC(O)OH.[3] This reaction then appears to proceed by

$$\begin{array}{l} OH+HC(O)OH\rightarrow H_2O+HCO_2 \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad H+CO_2 \end{array}$$

with overall abstraction of the H (or D) atom from the –OH (or –OD) group being the major pathway at room temperature.

References

[1] P. H. Wine, R. J. Astalos, and R. L. Mauldin III, J. Phys. Chem. **89**, 2620 (1985).

[2] G. S. Jolly, D. J. McKenney, D. L. Singleton, G. Paraskevopoulos, and A. R. Bossard, J. Phys. Chem. **90**, 6557 (1986).

[3] D. L. Singleton, G. Paraskevopoulos, R. S. Irwin, G. S. Jolly, and D. J. McKenney, J. Am. Chem. Soc. **110**, 7786 (1988).

[4] P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, Int. J. Chem. Kinet. **20**, 331 (1988).

[5] NASA Evaluation No. 12, 1997 (see references in Introduction).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

[7] C. Zetzsch and F. Stuhl, *Proceedings of the 2nd European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants*, edited by B. Versino and H. Ott (D. Riedel Publishing, Dordrecht, The Netherlands, 1982), pp. 129–137.

HO + $CH_3COOH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.3\times10^{-12}\exp[-(170\pm20)/T]$	240–440	Dagaut *et al.*, 1988[1]	FP-RF
$(7.4\pm0.6)\times10^{-13}$	298		
$(8.67\pm0.65)\times10^{-13}$	296.8	Singleton, Paraskevopoulos, and Irwin, 1989[2]	PLP-RA
$(5.63\pm0.44)\times10^{-13}$	326.2		
$(4.88\pm0.17)\times10^{-13}$	356.4		
$(4.09\pm0.14)\times10^{-13}$	396.8		
$(3.95\pm0.07)\times10^{-13}$	446.2		
Reviews and Evaluations			
$4.0\times10^{-13}\exp(200/T)$	240–450	NASA, 1997[3]	(a)
8×10^{-13}	298	IUPAC, 1997[4]	(b)

Comments

(a) The 298 K rate coefficient was the average of the data of Dagaut *et al.*[1] and Singleton *et al.*[2] The temperature dependence is between those reported by Dagaut *et al.*[1] and Singleton *et al.*[2]

(b) See Comments on Preferred Values.

Preferred Values

$k=8\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

At 298 K, the rate coefficients of Dagaut *et al.*[1] and Singleton *et al.*[2] are in reasonable agreement. However, at temperatures above 298 K, Dagaut *et al.*[1] observed the rate coefficient to increase with increasing temperature, while Singleton *et al.*[2] observed the rate coefficient to decrease in a non-Arrhenius manner with increasing temperature. At 400–440 K, the rate coefficients of Dagaut *et al.*[1] and Singleton *et al.*[2] disagree by a factor of 2.2.

The preferred 298 K rate coefficient is an average of the data of Dagaut *et al.*[1] and Singleton *et al.*[2] No recommendation is made regarding the temperature dependence. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[4] The rate coefficients of Singleton *et al.*[3] for the reactions of the HO radical with $CH_3C(O)OH$, $CD_3C(O)OH$, and $CD_3C(O)OD$ indicate that at room temperature the major reaction channel involves overall H-atom abstraction from the –OH bond:

$$HO+CH_3C(O)OH \rightarrow H_2O+CH_3CO_2$$

References

[1] P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, Int. J. Chem. Kinet. **20**, 331 (1988).

[2] D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, J. Am. Chem. Soc. **111**, 5248 (1989).

[3] NASA Evaluation No. 12, 1997 (see references in Introduction).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

HO + $C_2H_5COOH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.8\times10^{-12}\exp[-(120\pm30)/T]$	298–440	Dagaut *et al.*, 1988[1]	FP-RF
$(1.22\pm0.12)\times10^{-12}$	298		
$(1.07\pm0.05)\times10^{-12}$	298–445	Singleton, Paraskevopoulos, and Irwin, 1989[2]	PLP-RA
$(1.02\pm0.55)\times10^{-12}$	298		
Reviews and Evaluations			
1.16×10^{-12}	298–445	Atkinson, 1994[3]	(a)
1.2×10^{-12}	290–450	IUPAC, 1997[4]	(b)

Comments

(a) Derived from an average of all of the rate coefficients of Dagaut *et al.*[1] and Singleton *et al.*[2] These data[1,2] indicate that the rate coefficient is independent of temperature over the range 298–445 K.
(b) See Comments on Preferred Values.

Preferred Values

$k = 1.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–450 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The rate coefficients measured by Dagaut *et al.*[1] and Singleton *et al.*[2] are in good agreement and indicate that the rate coefficient for this reaction is independent of temperature over the range 298–445 K. The preferred value is an average of all of the rate coefficients of Dagaut *et al.*[1] and Singleton *et al.*,[2] combined with a zero temperature dependence, and is identical to that in our previous evaluation, IUPAC, 1997.[4] The reaction is expected to proceed by H-atom abstraction from the C–H bonds of the $-CH_3$ group and the O–H bond of the –C(O)OH group.

References

[1] P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, Int. J. Chem. Kinet. **20**, 331 (1988).
[2] D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, J. Am. Chem. Soc. **111**, 5248 (1989).
[3] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 2**, 1 (1994).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$HO + CH_3ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.4\pm0.4)\times10^{-14}$	298	Gaffney *et al.*, 1986[1]	DF-RF (a)
$8.8\times10^{-15}\exp[(1050\pm180)/T]$	298–393	Nielsen *et al.*, 1991[2]	PR-RA (b)
$(3.2\pm0.5)\times10^{-13}$	298±2		
$8.2\times10^{-13}\exp[-(1020\pm60)/T]$	221–414	Talukdar *et al.*, 1997[3]	PLP-LIF (c)
$(2.36\pm0.16)\times10^{-14}$	298		
$4.1\times10^{-13}\exp[-(604\pm121)/T]$	298–423	Shallcross *et al.*, 1997[4]	DF-RF (d)
$(4.7\pm1.0)\times10^{-14}$	298		
Relative Rate Coefficients			
$(3.8\pm1.0)\times10^{-13}$	303±2	Kerr and Stocker, 1986[5]	RR (e)
$(3.2\pm0.7)\times10^{-13}$	298±2	Nielsen *et al.*, 1991[2]	RR (f)
$(3.0\pm0.8)\times10^{-14}$	307±3	Kakesu *et al.*, 1997[6]	RR (g)
Reviews and Evaluations			
$5.0\times10^{-13}\exp(-890/T)$	220–420	NASA, 1997[7]	(h)
$1.0\times10^{-14}\exp(1060/T)$ (1 bar)	290–400	IUPAC, 1997[8]	(i)

Comments

(a) Conducted at 2.6–4.2 mbar (2.0 Torr to 3.2 Torr) of He.
(b) Conducted at 1 bar Ar.
(c) In addition to measuring rate coefficients for the reaction of the HO radical with CH_3ONO_2, rate coefficients were measured for the reactions of the HO radical with CD_3ONO_2 (298–409 K), the DO radical with CH_3ONO_2 (246–353 K) and the HO^{18} radical with CH_3ONO_2 (253–298 K). HO, HO^{18}, and DO radicals were generated by the pulsed laser photolysis of HONO at 355 nm and of O_3–H_2O mixtures at 266 nm, photolysis of O_3–H_2O^{18} mixtures at 266 nm, and photolysis of DONO at 355 nm and of O_3–D_2O mixtures at 266 nm, respectively. The diluent gas pressure was varied from 67 mbar (50 Torr) He plus 67 mbar (50 Torr) SF_6 to 133 mbar (100 Torr) He and to 400 mbar (300 Torr) SF_6, and up to 67 mbar (50 Torr) of O_2 was included in certain experiments. No effect of total pressure, nature of the diluent gas, or presence of O_2 on the measured rate coefficients was observed. The rate coefficients for the reactions of the HO^{18} radical with CH_3ONO_2 were essentially identical to those for the corresponding HO radical reaction, while the measured rate coefficients for the DO radical reaction were ~10–20% higher than the HO radical reaction. No

evidence for formation of HO radicals was observed from these HO^{18} and DO radical reactions. The rate coefficients for the reaction of the HO radical with CD_3ONO_2 were a factor of 3–4 lower than those for $HO+CH_3ONO_2$ over the temperature range studied (298–409 K).

(d) The rate coefficient at 298 K was measured over the pressure range 2.7–27 mbar (2–20 Torr) of He, with no effect of pressure being observed. Rate coefficients at 333–423 K were measured over the pressure range 1.3–4.0 mbar (1–3 Torr) of He.

(e) HO radicals were generated from the photolysis of HONO–air mixtures at atmospheric pressure. The concentrations of methyl nitrate and ethene (the reference organic) were measured by GC. The measured rate coefficient ratio of $k(\mathrm{HO+methyl\ nitrate})/k(\mathrm{HO+ethene})=0.046\pm0.011$ placed on an absolute basis by use of $k(\mathrm{HO+ethene})=8.32\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 303 K and 1 atm of air.[9]

(f) Relative rate method. HO radicals generated by the photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. The decays of CH_3ONO_2 and $(CH_3)_3CH$ were measured by GC. The rate coefficient ratio is placed on an absolute basis by use of $k(\mathrm{HO}+(CH_3)_3CH)=2.19\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[9]

(g) Relative rate method. HO radicals were generated by photolysis of O_3–H_2O–O_2 mixtures at atmospheric pressure at ~290–310 nm. Methyl nitrate and the reference compounds (methane, ethane, and HFC-152a) were monitored by GC. The measured rate coefficient ratios are placed on an absolute basis by use of rate coefficients of $k(\mathrm{HO}+CH_4)=2.15\times10^{-12}\exp(-1735/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation), $k(\mathrm{HO}+C_2H_6)=7.8\times10^{-12}\exp(-1025/T)$ cm^3 molecule^{-1}s^{-1} (this evaluation) and $k(\mathrm{HO}+CH_3CHF_2)=1.0\times10^{-12}\exp(-990/T)$cm^3 molecule^{-1} s^{-1}.[8] Value cited is the unweighted average, with a two standard deviation error limit.

(h) Based on the data of Talukdar *et al.*[2]

(i) Based on the absolute and relative rate studies of Kerr and Stocker[5] and Nielsen *et al.*[2]

Preferred Values

$k=2.3\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=4.0\times10^{-13}\exp(-845/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–300 K.

Reliability

$\Delta\log k=^{+0.5}_{-0.2}$ at 298 K.

$\Delta(E/R)=\pm400$ K.

Comments on Preferred Values

There are serious discrepancies between the room temperature rate coefficients of Gaffney *et al.*,[1] Talukdar *et al.*,[3] and Kakesu *et al.*[6] and those of Kerr and Stocker[5] and Nielsen *et al.*,[2] of a factor of 10–13. Additionally, the temperature dependencies of Nielsen *et al.*[2] and Talukdar *et al.*[3] differ by ~2000 K. The positive temperature dependence observed by Talukdar *et al.*[3] is supported qualitatively by the low-pressure absolute rate study of Shallcross *et al.*,[4] although the rate coefficients of Shallcross *et al.*[4] are a factor of ~1.3–2.0 higher than those of Talukdar *et al.*[3] over the temperature range 298–423 K. The reasons for these various discrepancies are not presently known, but we favor the results of the Talukdar *et al.*[3] study which are consistent with H– (or D–) atom abstraction to form H_2O+CH_2ONO. The extensive absolute study of Talukdar *et al.*[3] shows no effect of the measured rate coefficient on pressure or diluent gas (133 mbar He–400 mbar SF_6) nor on the presence or absence of up to 67 mbar of O_2. The experiments of Talukdar *et al.*[3] on the reactions $HO+CH_3ONO_2$, $HO^{18}+CH_3ONO_2$, $DO+CH_3ONO_2$ and $HO+CH_3ONO$ show no formation of HO radicals from the HO^{18} and DO radical reactions with CH_3ONO, and the deuterium isotope effect of $k_H/k_D\sim4$ at 298 K is totally consistent with H– (or D–) atom abstraction.

The preferred values are obtained from a unit-weighted least-squares analysis of the 221–298 K rate coefficients of Talukdar *et al.*[3] Because of the significant discrepancies between the various studies,[1–6] large uncertainty limits are assigned to the 298 K rate coefficient and the temperature dependence. Clearly, further absolute rate studies at atmospheric pressure of air are needed.

References

[1] J. S. Gaffney, R. Fajer, G. I. Senum, and J. H. Lee, Int. J. Chem. Kinet. **18**, 399 (1986).

[2] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).

[3] R. K. Talukdar, S. C. Herndon, J. B. Burkholder, J. M. Roberts, and A. R. Ravishankara, J. Chem. Soc. Faraday Trans. **93**, 2787 (1997).

[4] D. E. Shallcross, P. Biggs, C. E. Canosa-Mas, K. C. Clemitshaw, M. G. Harrison, M. Reyes López Alañón, J. A. Pyle, A. Vipond, and R. P. Wayne, J. Chem. Soc. Faraday Trans. **93**, 2807 (1997).

[5] J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).

[6] M. Kakesu, H. Bandow, N. Takenaka, Y. Maeda, and N. Washida, Int. J. Chem. Kinet. **29**, 933 (1997).

[7] NASA Evaluation No.12, 1997 (see references in Introduction).

[8] IUPAC, Supplement V, 1997 (see references in Introduction).

[9] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$HO + C_2H_5ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
4.7×10^{-14} exp[$(716\pm138)/T$]	298–373	Nielsen *et al.*, 1991[1]	PR-RA (a)
$(5.3\pm0.6)\times10^{-13}$	298±2		
3.68×10^{-14} exp($-1077/T$)	223–394	Talukdar *et al.*, 1997[2]	PLP-LIF (b)
$+5.32\times10^{-14}$ exp($126/T$)			
$(1.80\pm0.12)\times10^{-13}$	298		
3.80×10^{-12} exp[$-(699\pm140)/T$]	298–373	Shallcross *et al.*, 1997[3]	DF-RF (c)
$(3.30\pm0.66)\times10^{-13}$	298		
Relative Rate Coefficients			
$(4.9\pm2.1)\times10^{-13}$	303±2	Kerr and Stocker, 1986[4]	RR (d)
$(4.3\pm0.3)\times10^{-13}$	298±2	Nielsen *et al.*, 1991[1]	RR (e)
$(2.4\pm1.0)\times10^{-13}$	304±6	Kakesu *et al.*, 1997[5]	RR (f)
Reviews and Evaluations			
8.2×10^{-13} exp($-450/T$)	223–298	NASA, 1996[6]	(g)
4.4×10^{-14} exp($720/T$) [1 bar]	290–380	IUPAC, 1997[7]	(h)

Comments

(a) Conducted at 1 bar Ar.

(b) Extensive study of the reactions of ethyl nitrate with OH radicals (223–394 K), HO^{18} radicals (300 K) and DO radicals (229–378 K) HO, HO^{18}, and DO radicals were produced from the pulsed laser photolysis of HONO at 355 nm, of O_3–H_2O^{18} mixtures at 248 nm, and of DONO at 355 nm, respectively. The diluent gas and total pressures were He [67–400 mbar (50 Torr–300 Torr)], N_2 [400 mbar (300 Torr)], SF_6 [267 mbar (200 Torr)] or He-SF_6 [133–400 mbar (100–300 Torr)], and O_2 partial pressures of 67 mbar (50 Torr) were used in certain experiments. No effects on the measured rate coefficients were observed on varying the total pressure, the diluent gas, or the partial pressure of O_2. The measured rate coefficients for the reactions of the HO^{18} and DO radicals with ethyl nitrite were 11%–16% higher than that for the HO radical reaction, and no formation of HO radicals was observed in the HO^{18} and DO radical reactions.

(c) The rate coefficient at 298 K was measured over the pressure range 5.7–27 mbar (4.3–19.9 Torr) of He, with no effect of pressure being observed. The rate coefficients at 313 and 373 K were measured over the pressure range 1.3–4.0 mbar (1–3 Torr) of He.

(d) HO radicals generated by photolysis of HONO–air mixtures at atmospheric pressure. The concentrations of ethyl nitrate and ethene (the reference organic) were measured by GC. The measured rate coefficient ratio of k(HO+ethyl nitrate)/k(HO+ethene) $=0.059\pm0.025$ is placed on an absolute basis by use of a rate coefficient k(HO+ethene) $=8.32\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 303 K and atmospheric pressure of air.[8]

(e) HO radicals were generated by photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. The concentrations of ethyl nitrate and 2-methylpropane (the reference organic) were measured by GC, and the measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(HO+2-methylpropane) $=2.19\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[8]

(f) Relative rate method. HO radicals were generated by the photolysis of O_3–H_2O–O_2 mixtures at atmospheric pressure and at ~290–310 nm. The concentrations of ethyl nitrate and the reference compounds ethane and n-butane were measured by GC. The measured rate coefficient ratios are placed on an absolute basis by use of rate coefficients of k(HO+ethane) $=7.8\times10^{-12}$ exp($-1025/T$) cm^3 molecule^{-1} s^{-1} (this evaluation) and k(HO+n-butane) $=9.1\times10^{-12}$ exp($-395/T$) cm^3 molecule^{-1} s^{-1} (this evaluation). The value cited is the unweighted average with a two standard deviation error limit.

(g) Based on the absolute rate coefficients of Talukdar over the temperature range 223–298 K.

(h) Based on the data of Kerr and Stocker[4] and Nielsen *et al.*[1]

Preferred Values

$k=1.8\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=6.7\times10^{-13}$ exp($-395/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 230–300 K.

Reliability

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

$\Delta(E/R) = \pm400$ K.

Comments on Preferred Values

There are serious discrepancies between the absolute and relative rate studies of Kerr and Stocker[4] and Nielsen *et al.*[1] carried out at ~1 bar total pressure and the extensive absolute rate and relative rate studies of Talukdar *et al.*[2] and Kakesu *et al.*,[5] respectively, in both the room temperature rate coefficient[1,2,4] (a factor of 2.4–2.9) and the temperature dependence.[1,2] The positive temperature dependence observed by Talukdar *et al.*[2] is supported, qualitatively, by the low-pressure absolute rate study of Shallcross *et al.*,[3] although the rate coefficients of Shallcross *et al.*[3] are a factor of ~1.8 higher than those of Talukdar *et al.*[2] The reasons for these discrepancies are not known, but we favor the results of the extensive Talukdar *et al.*[2] study which are consistent with H– (or D–) atom abstraction. The study of Talukdar *et al.*[2] showed no effect of total pressure, diluent gas [ranging from 67 mbar (50 Torr) of He to 267 mbar (200 Torr) of SF_6 or 400 mbar (300 Torr) N_2] or the presence or absence of O_2 at a partial pressures of 67 mbar (50 Torr) on the measured rate coefficients.

While the study of Talukdar *et al.*[2] was not carried out in air at 1 bar pressure, the data obtained strongly suggest that the rate coefficient is consistent with an H-atom abstraction process and that the measured rate coefficients should be appropriate for atmospheric purposes. The Arrhenius plots of the HO and DO radical reactions exhibit significant curvature.[2] The preferred values are based on a unit-weighted least-squares fit of the 233–298 K rate coefficients of Talukdar *et al.*[2] to the Arrhenius expression, $k = A\ \exp(-B/T)$. Large uncertainty limits are assigned because of the discrepancies between the various studies[1–5] noted above. Further absolute rate studies conducted at atmospheric pressure of air are required.

References

[1] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).

[2] R. K. Talukdar, S. C. Herndon, J. B. Burkholder, J. M. Roberts, and A. R. Ravishankara, J. Chem. Soc. Faraday Trans. **93**, 2787 (1997).

[3] D. E. Shallcross, P. Biggs, C. E. Canosa-Mas, K. C. Clemitshaw, M. G. Harrison, M. Reyes López Alañón, J. A. Pyle, A. Vipond, and R. P. Wayne, J. Chem. Soc. Faraday Trans. **93**, 2807 (1997).

[4] J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).

[5] M. Kakesu, H. Bandow, H. Takenaka, Y. Maeda, and N. Washida, Int. J. Chem. Kinet. **29**, 933 (1997).

[6] NASA Evaluation No. 12, 1997 (see references in Introduction).

[7] IUPAC, Supplement V, 1997 (see references in Introduction).

[8] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

HO + 1-$C_3H_7ONO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.0\times10^{-13}\ \exp[(140\pm144)/T]$	298–368	Nielsen *et al.*, 1991[1]	PR-RA (a)
$(8.2\pm0.8)\times10^{-13}$	298±2		
Relative Rate Coefficients			
$(7.2\pm2.3)\times10^{-13}$	303±2	Kerr and Stocker, 1986[2]	RR (b)
$(6.0\pm1.0)\times10^{-13}$	298±2	Atkinson and Aschmann, 1989[3]	RR (c)
$(7.2\pm0.8)\times10^{-13}$	298±2	Nielsen *et al.*, 1991[1]	RR (d)
Reviews and Evaluations			
7.3×10^{-13} (1 bar)	290–370	IUPAC, 1997[4]	(e)

Comments

(a) Carried out in 1 bar Ar.

(b) HO radicals were generated by the photolysis of HONO–air mixtures at atmospheric pressure. The decay rates of 1-propyl nitrate and ethene (the reference organic) were measured by GC and rate coefficient ratio $k(\text{HO}+1\text{-propyl nitrate})/k(\text{HO}+\text{ethene}) = 0.086 \pm 0.027$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO}+\text{ethene}) = 8.32\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 303 K and atmospheric pressure of air.[5]

(c) HO radicals were generated by the photolysis of CH_3ONO at ~1 bar air at >300 nm. Experiments were carried out in a 6400 L Teflon chamber. The concentrations of 1-propyl nitrate and cyclohexane (the reference organic) were measured by GC, and irradiations in the absence of CH_3ONO allowed the photolysis of 1-propyl nitrate to be accurately taken into account in the data analysis. The measured rate coefficient ratio of $k(\text{HO}+1\text{-propyl nitrate})/k(\text{HO}+\text{cyclohexane}) = 0.083\pm0.013$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO}+\text{cyclohexane}) = 7.21\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.[5]

(d) HO radicals were generated from the photolysis of CH_3ONO in 1 bar air at >290 nm. The concentrations of 1-propyl nitrate and 2-methylpropane (the reference organic) were measured by GC. The measured rate coefficient ratio k(HO+1-propyl nitrate)/k(HO +2-methylpropane) is placed on an absolute basis by use of a rate coefficient of k(HO+2-methylpropane) $=2.19\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.[5]

(e) Based on the data of Kerr and Stocker,[2] Atkinson and Aschmann,[3] and Nielsen *et al.*[1]

Preferred Values

$k=6\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar air.

Reliability

$\Delta \log k=\pm0.3$ at 298 K (1 bar).

Comments on Preferred Values

The absolute and relative rate coefficients of Kerr and Stocker,[2] Atkinson and Aschmann,[3] and Nielsen *et al.*[1] are in reasonable agreement at room temperature. All studies have been carried out at ~1 bar pressure.

The absolute rate coefficient study of Talukdar *et al.*[6] for the HO radical reactions with CH_3ONO_2 and $C_2H_5ONO_2$ is in serious disagreement (by a factor of 13–16 for CH_3ONO_2 and a factor of 2.6–2.9 for $C_2H_5ONO_2$) with the rate coefficients from the studies of Kerr and Stocker[2] and Nielsen *et al.*,[1] while for 2-$C_3H_7ONO_2$ the 298 K rate coefficients of Talukdar *et al.*[6] and Atkinson and Aschmann[3] disagree by 37% (suggesting for one that the discrepancies decrease as the reactivity of the alkyl nitrate increases). Accordingly, the 298 K rate coefficient of Atkinson and Aschmann[3] is used for the preferred value, and no temperature dependence is recommended (note that by analogy with the reaction of the OH radical with 2-propyl nitrate (this evaluation), the temperature dependence of the rate coefficient is likely to be small). That 1-propyl nitrate is more reactive than 2-propyl nitrate is expected from structure–reactivity relationships based on assuming that the reaction proceeds by H-atom abstraction, as concluded by Talukdar *et al.*[6] for methyl nitrate, ethyl nitrate, and 2-propyl nitrate.

References

[1] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).

[2] J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).

[3] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **21**, 1123 (1989).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

[5] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

[6] R. K. Talukdar, S. C. Herndon, J. B. Burkholder, J. M. Roberts, and A. R. Ravishankara, J. Chem. Soc. Faraday Trans. **93**, 2787 (1997).

HO + 2-$C_3H_7ONO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.3\times10^{-12}\exp(-1250/T)$ $+2.5\times10^{-13}\exp(-32/T)$	233–395	Talukdar *et al.*, 1997[1]	PLP-LIF (a)
$(2.88\pm0.19)\times10^{-13}$	298		
Relative Rate Coefficients			
$(1.74\pm0.44)\times10^{-13}$	299±2	Atkinson *et al.*, 1982[2]	RR (b)
$(5.5\pm2.2)\times10^{-13}$	295±2	Becker and Wirtz, 1989[3]	RR (c)
$(3.97\pm0.51)\times10^{-13}$	298±2	Atkinson and Aschmann, 1989[4]	RR (d)
Reviews and Evaluations			
4.9×10^{-13}	298	IUPAC, 1997[5]	(e)

Comments

(a) Experiments were carried out as a function of total pressure and with different diluent gases (133 mbar He to 400 mbar SF_6) and with up to 80 mbar O_2 present. No effect of pressure, diluent gas or presence or absence of O_2 on the measured rate coefficients were observed. Rate coefficients for the reaction of HO^{18} and DO radicals with 2-propyl nitrate were also measured over the temperature ranges 233–298 K and 230–403 K, respectively, with 298 K rate coefficients of $(3.15\pm0.20)\times10^{-13}$ cm^3 molecule^{-1} s^{-1} and $(3.6\pm0.4)\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, respectively.

(b) HO radicals were generated from the photolysis of CH_3ONO in ~1 bar air at >300 nm. Experiments were carried out in an ~75 L Teflon chamber, and concurrent photolysis of 2-propyl nitrate was indicated from the data analysis. The concentrations of 2-propyl nitrate and cyclohexane (the reference organic) were measured by GC. The measured rate coefficient ratio of

k(HO+2-propyl nitrate/k(HO+cyclohexane)=0.024 ±0.006 is placed on an absolute basis by use of a rate coefficient of k(HO+cyclohexane)=7.24×10^{-12} cm^3 molecule^{-1} s^{-1} at 299 K.[6]

(c) HO radicals were generated from the photolysis of CH_3ONO in 1 bar air at 280–450 nm. Experiments were carried out in a 36.5 L quartz chamber, and photolysis of 2-propyl nitrate was indicated from the data analysis. The concentrations of 2-propyl nitrate and n-butane (the reference organic) were measured by GC-MS and GC, respectively. The measured rate coefficient ratio of k(HO+2-propyl nitrate)/k(HO+n-butane)=0.23±0.09 is placed on an absolute basis by use of a rate coefficient of k(HO+n-butane) =2.4×10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K (this evaluation).

(d) HO radicals were generated by the photolysis of CH_3ONO in ~1 bar air at >300 nm. Experiments were carried out in a 6400 L Teflon chamber. The concentrations of 2-propyl nitrate and cyclohexane (the reference organic) were measured by GC, and irradiations in the absence of CH_3ONO allowed the photolysis of 2-propyl nitrate to be accurately taken into account in the data analysis. The measured rate coefficient ratio of k(HO+2-propyl nitrate)/k(HO+cyclohexane)=0.055 ±0.007 is placed on an absolute basis by use of a rate coefficient of k(HO+cyclohexane)=7.21×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.[6] This study supersedes the earlier study of Atkinson *et al.*[2]

(e) Obtained from an average of the rate coefficients of Becker and Wirtz[3] and Atkinson and Aschmann.[4]

Preferred Values

$k=2.9\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=6.2\times10^{-13}$ exp($-230/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 230–300 K.

Reliability

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

$\Delta(E/R)=\pm300$ K

Comments on Preferred Values

The preferred values are based on the absolute 233–300 K rate coefficients of Talukdar *et al.*[1] The extensive study of Talukdar *et al.*[1] provided no evidence for the rate coefficient k to depend on total pressure, nature of the diluent gas, or the presence of O_2 at pressures up to 80 mbar (60 Torr). Additionally, the use of DO radicals showed no evidence for the formation of HO radicals as a reaction product. However, as noted in the data sheets for the reactions of the HO radical with CH_3ONO_2, and $C_2H_5ONO_2$, the experiments of Talukdar *et al.*[1] were not actually carried out in air at 1 bar total pressure.

Arrhenius plots of the rate coefficients for the reactions of HO, HO^{18}, and DO radicals with 2-propyl nitrate exhibit significant curvature (especially pronounced for the DO radical reaction for which the measured rate coefficient was independent of temperature over the range 230–269 K). The measured temperature dependencies at around 298 K and below are quite small, although it may be noted that the temperature dependencies, $k=A$ exp($-B/T$), of the HO radical reaction with the similarly slowly reacting compounds methanol, acetone and 2,3-butanedione (biacetyl) at ~265 K are $B\approx360$, 520, and 336 K, respectively (this evaluation and Ref. 7). The room temperature relative rate coefficient of Atkinson and Aschmann[4] (which supersedes the earlier data of Atkinson *et al.*[2]) is 37% higher than the recommended 298 K rate coefficient, which may be considered reasonable agreement because of the low rate coefficient (on the low end of those reported by that research group) and hence small fraction of 2-propyl nitrate reacted during the experiments. The relative rate coefficient of Becker and Wirtz[3] is almost a factor of 2 higher than the recommendations, but has high cited uncertainties.

We attach rather large uncertainties to the recommended values of the 298 K rate coefficient and E/R until the data of Talukdar *et al.*[1] are confirmed by absolute techniques in air at 1 bar pressure.

References

[1] R. K. Talukdar, S. C. Herndon, J. B. Burkholder, J. M. Roberts, and A. R. Ravishankara, J. Chem. Soc. Faraday Trans. **93**, 2787 (1997).
[2] R. Atkinson, S. M. Aschmann, W. P. L. Carter, and A. M. Winer, Int. J. Chem. Kinet. **14**, 919 (1982).
[3] K. H. Becker and K. Wirtz, J. Atmos. Chem. **9**, 419 (1989).
[4] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **21**, 1123 (1989).
[5] IUPAC, Supplement V, 1997 (see references in Introduction).
[6] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).
[7] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 2**, 1 (1994).

$HO + 1\text{-}C_4H_9ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.74 \pm 0.19) \times 10^{-12}$	298 ± 2	Nielsen *et al.*, 1991[1]	PR-RA (a)
Relative Rate Coefficients			
$(1.35 \pm 0.11) \times 10^{-12}$	299 ± 2	Atkinson *et al.*, 1982[2]	RR (b,c)
$(1.72 \pm 0.19) \times 10^{-12}$	298 ± 2	Atkinson and Aschmann, 1989[3]	RR (b,d)
$(1.52 \pm 0.08) \times 10^{-12}$	298 ± 2	Nielsen *et al.*, 1991[1]	RR (b,e)
Reviews and Evaluations			
1.71×10^{-12}	298	Atkinson, 1994[4]	(f)

Comments

(a) Carried out at a total pressure of 1 bar Ar.

(b) HO radicals were generated by the photolysis of CH_3ONO in air at atmospheric pressure (0.97–1.0 bar). The concentrations of 1-butyl nitrate and the reference organic were measured by GC.

(c) The measured rate coefficient ratio of k(HO + 1-butyl nitrate)/k(HO+cyclohexane)$= 0.187 \pm 0.014$ is placed on an absolute basis by use of a rate coefficient of k(HO+cyclohexane)$= 7.24 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 299 K.[5] Experiments were carried out in an ~ 75 L Teflon chamber, and the data were interpreted as involving concurrent photolysis of 1-butyl nitrate.

(d) Experiments were carried out in a 6400 L Teflon chamber, and irradiations were also carried out in the absence of CH_3ONO, allowing the photolysis rate to be accurately allowed for in the data analysis. The measured rate coefficient ratio of k(HO+1-butyl nitrate)/k(HO+cyclohexane)$= 0.237 \pm 0.025$ is placed on an absolute basis by use of a rate coefficient of k(HO +cyclohexane)$= 7.21 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.[5] These data supersede those of Atkinson *et al.*[2]

(e) The measured rate coefficient ratio k(HO + 1-butyl nitrate)/k(HO+2-methylpropane) is placed on an absolute basis by use of a rate coefficient of k(HO+2-methylpropane)$= 2.19 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.[5]

(f) Based on an average of the absolute and relative rate coefficients of Atkinson and Aschmann[3] and Nielsen *et al.*[1]

Preferred Values

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

Reliability

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

Comments on Preferred Values

The absolute and relative rate coefficients of Atkinson and Aschmann[3] (which supersedes the earlier data of Atkinson *et al.*[2]) and Nielsen *et al.*[1] are in good agreement. The preferred value is an average of the absolute and relative rate constants of Atkinson and Aschmann[3] and Nielsen *et al.*[1] By analogy with the reaction of the HO radical with 2-propyl nitrate (this evaluation), the temperature dependence of the rate coefficient at temperatures ≤300 K is likely to be small.

References

[1] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).

[2] R. Atkinson, S. M. Aschmann, W. P. L. Carter, and A. M. Winer, Int. J. Chem. Kinet. **14**, 919 (1982).

[3] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **21**, 1123 (1989).

[4] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 2**, 1 (1994).

[5] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$HO + 2\text{-}C_4H_9ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(6.6 \pm 1.0) \times 10^{-13}$	299 ± 2	Atkinson *et al.*, 1982[1]	RR (a,b)
$(8.9 \pm 1.6) \times 10^{-13}$	298 ± 2	Atkinson and Aschmann, 1989[2]	RR (a,c)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in 1 atm of air. The concentrations of 2-butyl nitrate and the reference organic were measured by GC.

(b) Experiments were carried out in an ~75 L Teflon chamber, and the data were interpreted as involving concurrent photolysis of 2-butyl nitrate. The measured rate constant ratio of k(HO+2-butyl nitrate)/k(HO+cyclohexane)$=0.091\pm0.013$ is placed on an absolute basis by use of a rate coefficient of k(HO+cyclohexane)$=7.24\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 299 K.[3]

(c) Experiments were carried out in a 6400 L Teflon chamber, and irradiations were also carried out in the absence of CH_3ONO allowing the photolysis rate to be accurately allowed for in the data analysis. The measured rate coefficient ratio of k(HO+2-butyl nitrate)/k(HO+cyclohexane)$=0.123\pm0.021$ is placed on an absolute basis by use of a rate coefficient of k(HO+cyclohexane)$=7.21\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.[3] These data supersede those of Atkinson *et al.*[1]

Preferred Values

$k=9\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is based on the rate coefficient of Atkinson and Aschmann,[2] which supersedes the earlier study of Atkinson *et al.*[1] By analogy with the reaction of the HO radical with 2-propyl nitrate (this evaluation), the temperature dependence of the rate coefficient at temperatures $\leqslant300$ K is likely to be small.

References

[1] R. Atkinson, S. M. Aschmann, W. P. L. Carter, and A. M. Winer, Int. J. Chem. Kinet. **14**, 919 (1982).
[2] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **21**, 1123 (1989).
[3] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

HO + $CH_3C(O)OONO_2$ → products

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leqslant1.7\times10^{-13}$	299±1	Winer *et al.*, 1977[1]	FP-RF
$1.23\times10^{-12}\exp[-(651\pm229)/T]$	273–297	Wallington, Atkinson, and Winer, 1984[2]	FP-RF
$(1.37\pm0.05)\times10^{-13}$	297±2		
$(7.5\pm1.4)\times10^{-14}$	298	Tsalkani *et al.*, 1988[3]	DF-EPR
$<3.0\times10^{-14}$	298	Talukdar *et al.*, 1995[4]	FP/PLP-LIF (a)
Reviews and Evaluations			
$<4\times10^{-14}$	298	NASA, 1997[5]	(b)
$9.5\times10^{-13}\exp(-650/T)$	270–300	IUPAC, 1997[6]	(c)

Comments

(a) Experiments were carried out over the temperature range 253–298 K, using the pulsed laser photolysis of HONO at 355 nm, the pulsed laser photolysis of O_3–H_2O mixtures at 266 nm, or the flash photolysis of H_2O at 165–185 nm. The measured HO radical decay rates corresponded to rate coefficients in the range $(0.82-2.50)\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} with no obvious dependence on temperature. The measured HO radical decay rates were attributed to the reaction of HO radicals with HCHO impurity, and a conservative upper limit to the rate coefficient k was cited (see table).

(b) Based on the data of Talukdar *et al.*[4]

(c) Based on the data of Wallington *et al.*[2] and Tsalkani *et al.*[3]

Preferred Values

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

Comments on Preferred Values

The preferred upper limit to the 298 K rate coefficient is the upper limit reported by Talukdar *et al.*[4] from an extensive and careful study. The higher rate coefficients measured by Wallington *et al.*[2] and Tsalkani *et al.*[3] were almost certainly due to the presence of reactive impurities.

References

[1] A. M. Winer, A. C. Lloyd, K. R. Darnall, R. Atkinson, and J. N. Pitts, Jr., Chem. Phys. Lett. **51**, 221 (1977).

[2] T. J. Wallington, R. Atkinson, and A. M. Winer, Geophys. Res. Lett. **11**, 861 (1984).

[3] N. Tsalkani, A. Mellouki, G. Poulet, G. Toupance, and G. Le Bras, J. Atmos. Chem. **7**, 409 (1988).

[4] R. K. Talukdar, J. B. Burkholder, A.-M. Schmoltner, J. M. Roberts, R. R. Wilson, and A. R. Ravishankara, J. Geophys. Res. **100**, 14163 (1995).

[5] NASA Evaluation No. 12, 1997 (see references in Introduction).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

$HO + CH_3COCH_2ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$<4.1\times10^{-13}$	298±2	Zhu, Barnes, and Becker, 1991[1]	(a)
Reviews and Evaluations			
$<1\times10^{-12}$	298	IUPAC, 1997[2]	(b)

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of $CH_3ONO-NO-N_2-O_2$ mixtures at 1 bar pressure. The concentrations of $CH_3COCH_2ONO_2$ and n-butane were measured during the experiments by GC, and the measured rate constant ratio of $k(CH_3COCH_2ONO_2)/k(n\text{-butane})<0.17$ is placed on an absolute basis by use of a rate coefficient of $k(n\text{-butane})=2.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) See Comments on Preferred Values.

Preferred Values

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

Comments on Preferred Values

The preferred value is based on the sole study of Zhu *et al.*,[1] but with a higher upper limit to reflect additional uncertainties, and is identical to that in our previous evaluation, IUPAC, 1997.[2]

References

[1] T. Zhu, I. Barnes, and K. H. Becker, J. Atmos. Chem. **13**, 301 (1991).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$HO + HCN \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.2\times10^{-13}\exp(-400/T)$	296–433	Fritz *et al.*, 1984[1]	FP-RA (a)
$(3\pm1)\times10^{-14}$	298		
Reviews and Evaluations			
$1.2\times10^{-13}\exp(-400/T)$	290–440	NASA, 1997[2]	(b)
$1.2\times10^{-13}\exp(-400/T)$ (1 bar)	290–440	IUPAC, 1997[3]	(c)

Comments

(a) The measured rate coefficients were observed to be pressure dependent over the range ~13–600 mbar (~10–450 Torr) of N_2 diluent. The cited rate coefficients are those extrapolated to the high-pressure limit (k_∞).

(b) Based on the data of Fritz *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

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

$k = 1.2 \times 10^{-13} \exp(-400/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 290–440 K at 1 bar.

Reliability

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

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

Comments on Preferred Values

The preferred values are those of Fritz *et al.*[1] with wider error limits. The rate coefficient increases with increasing pressure over this temperature range, and the rate coefficients cited are those extrapolated by Fritz *et al.*[1] to the high-pressure limit. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[3]

The reaction proceeds by HO radical addition over this temperature range. At higher temperatures the available rate coefficient data indicate a direct abstraction reaction.[4]

References

[1] B. Fritz, K. Lorenz, W. Steinert, and R. Zellner, Oxid. Comm. **6**, 363 (1984).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).
[4] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 1**, 1 (1989).

$HO + CH_3CN \rightarrow$ products

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.3) \times 10^{-14}$	295±2	Poulet *et al.*, 1984[1]	DF-EPR
$(8.6 \pm 1) \times 10^{-14}$	393		
$6.28 \times 10^{-13} \exp(-1030/T)$	250–363	Kurylo and Knable, 1984[2]	FP-RF
$(1.94 \pm 0.37) \times 10^{-14}$	298		
$1.1 \times 10^{-12} \exp[-(1130 \pm 90)/T]$	256–388	Hynes and Wine, 1991[3]	PLP-LIF (a)
$(2.48 \pm 0.38) \times 10^{-14}$	298		
Reviews and Evaluations			
$7.8 \times 10^{-13} \exp(-1050/T)$	250–390	NASA, 1997[4]	(b)
$8.1 \times 10^{-13} \exp(-1080/T)$	250–390	IUPAC, 1997[5]	(c)

Comments

(a) No definitive evidence for a pressure dependence of the rate coefficient for the $HO + CH_3CN$ reaction was observed over the pressure range 61–933 mbar (46–700 Torr) of N_2 diluent or 40–840 mbar (30–630 Torr) of He diluent. In the presence of O_2, the HO radical decays were nonexponential indicating regeneration of HO radicals.

(b) The room temperature rate coefficient was based on the absolute rate coefficients of Poulet *et al.*,[1] Kurylo and Knable,[2] Rhäsa (unpublished data, 1983), and Hynes and Wine,[3] and the temperature dependence was derived from the studies of Kurylo and Knable,[2] the 295–391 K data of Rhäsa (unpublished data, 1983) and Hynes and Wine.[3]

(c) See Comments on Preferred Values.

Preferred Values

$k = 2.2 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K (1 bar).

$k = 8.1 \times 10^{-13} \exp(-1080/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 250–390 K at 1 bar.

Reliability

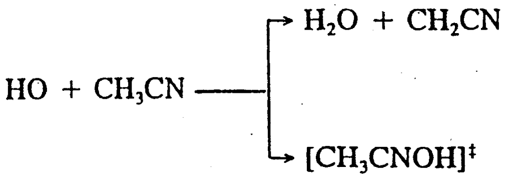
$\Delta \log k = \pm 0.15$ at 298 K.

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

Comments on Preferred Values

The preferred 298 K rate coefficient is a unit-weighted average of the rate coefficients of Poulet *et al.*,[1] Kurylo and Knable,[2] and Hynes and Wine.[3] The temperature dependence is the mean of those determined by Kurylo and Knable[2] and Hynes and Wine.[3] The mechanism and products of this reaction are not understood at present. Hynes and Wine[3] observed no definitive evidence for a pressure dependence of the rate coefficient for the $HO + CH_3CN$ reaction in N_2 or He diluent over the pressure ranges 61–933 mbar (46–700 Torr) or 40–840 mbar (30–630 Torr), respectively. In the presence of O_2, the HO radical decays were nonexponential,[3] indicating regeneration of HO radicals. Combined with analogous data for the reactions of HO radicals with CD_3CN [for which the rate coefficient was pressure dependent over the pressure range 53–923 mbar (40–692 Torr) of N_2 diluent][3] and of DO radicals with CH_3CN and CD_3CN,[3] it appears that the initial

HO radical reaction proceeds by H-atom abstraction from the $-CH_3$ group and HO radical addition to the –CN group.[3]



$$HO + CH_3CN \rightarrow \begin{cases} H_2O + CH_2CN \\ [CH_3CNOH]^{\ddagger} \end{cases}$$

Subsequent reactions of the addition adduct in the presence of O_2 then lead to the regeneration of HO radicals. In view of the possibility of a pressure dependence of the 298 K rate coefficient at low total pressures[3] (≤0.1 bar), the preferred values, which are identical to those in our previous evaluation, IUPAC, 1997,[5] are applicable to atmospheric conditions.

References

[1] G. Poulet, G. Laverdet, J. L. Jourdain, and G. Le Bras, J. Phys. Chem. **88**, 6259 (1984).

[2] M. J. Kurylo and G. L. Knable, J. Phys. Chem. **88**, 3305 (1984).

[3] A. J. Hynes and P. H. Wine, J. Phys. Chem. **95**, 1232 (1991).

[4] NASA Evaluation No. 12, 1997 (see references in Introduction).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

$HO_2+CH_3O_2 \rightarrow O_2+CH_3OOH$

$\Delta H° = -156$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
7.7×10^{-14} exp[(1296±364)/T]	274–338	Cox and Tyndall, 1980[1]	MM-AS (a)
$(6.5\pm1.0)\times10^{-12}$	298		
$(5.4\pm1.1)\times10^{-12}$	300	Jenkin *et al.*, 1988[2]	MM-IR-AS (b)
3.0×10^{-13} exp[(720±100)/T]	228–380	Dagaut, Wallington, and Kurylo, 1988[3]	FP-AS (c)
$(2.9\pm0.4)\times10^{-12}$	298		
$(4.8\pm0.2)\times10^{-12}$	300	Moortgat *et al.*, 1989[4]	MM-IR-AS (d)
4.4×10^{-13} exp[(780±55)/T]	248–573	Lightfoot, Veyret, and Lesclaux, 1990[5]	FP-AS (e)
$(6.2\pm1.0)\times10^{-12}$	298		
2.9×10^{-13} exp[(862±44)/T]	248–700	Lightfoot *et al.*, 1991[6]	(f)
Reviews and Evaluations			
5.6×10^{-13} exp(640/T)	228–573	Wallington, Dagaut, and Kurylo, 1992[7]	(g)
4.1×10^{-13} exp(790/T)	230–680	Lightfoot *et al.*, 1992[8]	(h)
3.8×10^{-13} exp(800/T)	228–573	NASA, 1997[9]	(i)
3.8×10^{-13} exp(780/T)	225–580	IUPAC, 1997[10]	(j)

Comments

(a) MM study of photolysis of Cl_2 in the presence of CH_4–H_2–O_2 mixtures at 1 bar pressure. CH_3O_2 and HO_2 radicals were monitored by absorption at 250 and 210 nm respectively.

(b) MM study of photolysis of Cl_2 in the presence of CH_4–H_2O_2–O_2 mixtures. HO_2 radicals were monitored by IR absorption with a tunable diode laser and CH_3O_2 monitored by UV absorption at 260 nm. $\sigma(CH_3O_2) = 3.53\times10^{-18}$ cm^2 molecule^{-1} was determined at 260 nm. k determined from observed perturbation of the second-order kinetics of the HO_2 radical self-reaction by the presence of CH_3O_2 in large excess. Experiments were carried out at a total pressure of 13 mbar (10 Torr). Similar experiments on mixtures of Cl_2–H_2–CH_4–O_2 were performed at 1 bar (760 Torr) total pressure and 303 K and yielded $k = (6.8\pm0.9)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, which was taken as confirmation of the value obtained at 13 mbar (10 Torr).

(c) FP-UV absorption study involving Cl_2–CH_3OH–CH_4–O_2–N_2 mixtures at total pressures of 130 mbar (100 Torr); $\sigma(HO_2)$ and $\sigma(CH_3O_2)$ were determined over the wavelength range 215 nm to 280 nm. At 250 nm $\sigma(CH_3O_2) = 3.3\times10^{-18}$ cm^2 molecule^{-1} was determined. First- or second-order kinetic conditions were not obtainable for either HO_2 or CH_3O_2 and k was determined from computer modeling of the absorption decay curves.

(d) Study of the photooxidation of CH_3CHO at 930 mbar (700 Torr), with double multipath spectrometer, combining both IR and UV absorption spectrometry for monitoring reactants and products, together with modulated photolysis for transient detection. Transient absorptions were assigned to peroxy radicals and the rate coefficient was obtained from kinetic analysis by computer simulation.

(e) FP-UV absorption study of Cl_2–CH_3OH–CH_4–O_2–N_2 mixtures at pressure of 160 or 1000 mbar (120 or 760 Torr). Revised cross-section data were used, $\sigma(HO_2) = 5.3\times10^{-18}$ cm^2 molecule^{-1} at 210 nm and $\sigma(CH_3O_2) = 3.6\times10^{-18}$ cm^2 molecule^{-1} at 260 nm.

(f) FP-UV absorption study of Cl_2–CH_3OH–CH_4–O_2–N_2 mixtures at 1 bar (760 Torr) and over the temperature range 600–719 K. The temperature-dependent rate coefficient listed above was derived by the authors from a re-analysis of all of their data, including previous studies from flash photolysis experiments.

(g) Derived from an analysis of the data of Cox and Tyndall,[1] McAdam *et al.*,[11] Kurylo *et al.*,[12] Jenkin *et al.*,[2] Dagaut *et al.*,[3] Moortgat *et al.*,[4] and Lightfoot *et al.*[5]

(h) k_{298} is an average value of the data of Cox and Tyndall,[1] McAdam *et al.*,[11] Jenkin *et al.*,[2] Dagaut *et al.*,[3] Moortgat *et al.*,[4] and Lightfoot *et al.*[5]

(i) k_{298} is the averaged value of data from Cox and Tyndall,[1] McAdam *et al.*,[11] Kurylo *et al.*,[12] Jenkin *et al.*,[2] Moortgat *et al.*,[4] and Lightfoot *et al.*[5] E/R derived from the data of Cox and Tyndall,[1] Dagaut *et al.*,[3] and Lightfoot *et al.*[5]

(j) See Comments on Preferred Values.

Preferred Values

$k = 5.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.8\times10^{-13}\exp(780/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 225–580 K.

Reliability

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

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

Comments on Preferred Values

The discrepancies in the data for this reaction, due in part to the different values of the UV absorption cross sections used in various studies,[9,10] remain unresolved.

The preferred rate coefficient at 298 K, which is unchanged from our last evaluation,[10] is the mean of the values of Cox and Tyndall,[1] Jenkin *et al.*,[2] Dagaut *et al.*,[3] Moortgat *et al.*,[4] and Lightfoot *et al.*[5] The recommended temperature coefficient is that reported by Lightfoot *et al.*,[5] selected on the basis of their wider range of temperatures than previous studies.[1,3] The *A* factor was then adjusted to fit the preferred value of k_{298}. The preferred rate parameters are in agreement with the most recent NASA recommendation.[9]

The studies of Kurylo *et al.*,[11] Jenkin *et al.*,[2] and Lightfoot *et al.*[5] show that the room temperature rate coefficient is independent of pressure over the range 13–1000 mbar (10–760 Torr).

The possibility of a second reaction channel, yielding $HCHO + H_2O + O_2$, discussed by Jenkin *et al.*,[2] receives some indirect support from the study of Moortgat *et al.*[4] They calculated a rate coefficient of $k(HO_2 + CH_3O_2 \rightarrow O_2 + CH_3OOH) = 3.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at room temperature from the computer simulation of the rate of formation of CH_3OOH. Since this is lower than their value based on the rate of decay of the peroxy radicals, they concluded that there could be an additional product channel. More direct information concerning the possible second channel comes from studies[13,14] of the products of the $HO_2 + CH_3O_2$ reaction, by FTIR spectroscopy. Over the pressure range 20–930 mbar (15–700 Torr) Wallington[13] has shown that $(92\pm5)\%$ of the $HO_2 + CH_3O_2$ reaction produces $O_2 + CH_3OOH$ and Wallington and Hurley[15] have shown that the reaction between HO_2 and CD_3O_2 radicals produces only $O_2 + CD_3OOH$.

References

[1] R. A. Cox and G. S. Tyndall, J. Chem. Soc. Faraday Trans. 2 **76**, 153 (1980).

[2] M. E. Jenkin, R. A. Cox, G. D. Hayman, and L. J. Whyte, J. Chem. Soc. Faraday Trans. 2 **84**, 913 (1988).

[3] P. Dagaut, T. J. Wallington, and M. J. Kurylo, J. Phys. Chem. **92**, 3833 (1988).

[4] G. K. Moortgat, R. A. Cox, G. Schuster, J. P. Burrows, and G. S. Tyndall, J. Chem. Soc. Faraday Trans. 2 **85**, 809 (1989).

[5] P. D. Lightfoot, B. Veyret, and R. Lesclaux, J. Phys. Chem. **94**, 708 (1990).

[6] P. D. Lightfoot, P. Roussel, F. Caralp, and R. Lesclaux, J. Chem. Soc. Faraday Trans. **87**, 3213 (1991).

[7] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).

[8] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).

[9] NASA Evaluation No. 12, 1997 (see references in Introduction).

[10] IUPAC, Supplement V, 1997 (see references in Introduction).

[11] K. McAdam, B. Veyret, and R. Lesclaux, Chem. Phys. Lett. **133**, 39 (1987).

[12] M. J. Kurylo, P. Dagaut, T. J. Wallington, and D. M. Neuman, Chem. Phys. Lett. **139**, 513 (1987).

[13] T. J. Wallington, J. Chem. Soc. Faraday Trans. **87**, 2379 (1991).

[14] T. J. Wallington and S. M. Japar, Chem. Phys. Lett. **167**, 513 (1990).

[15] T. J. Wallington and M. D. Hurley, Chem. Phys. Lett. **193**, 84 (1992).

$$HO_2 + HOCH_2O_2 \rightarrow O_2 + HOCH_2O_2H \quad (1)$$
$$\rightarrow O_2 + HCOOH + H_2O \quad (2)$$

$\Delta H°(2) = -473.1$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.6 \times 10^{-15} \exp[(2300 \pm 1100)/T]$ $(1.2 \pm 0.4) \times 10^{-11}$	275–333 295	Veyret *et al.*, 1989[1]	FP-AS (a)
$(1.2 \pm 0.3) \times 10^{-11}$	298	Burrows *et al.*, 1989[2]	MM-IR (b)
Branching Ratios			
$k_2/k = 0.40 \pm 0.15$	298	Burrows *et al.*, 1989[2]	MM-IR (c)
Reviews and Evaluations			
$5.6 \times 10^{-15} \exp(2300/T)$	275–335	IUPAC, 1997[3]	(d)

Comments

(a) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2 at total pressures of 110–230 mbar (85–170 Torr), with time-resolved absorption spectroscopy for HO_2 and $HOCH_2O_2$ radicals. The rate coefficient k was obtained from a computer simulation of the absorption profiles based on a mechanism of nine elementary reactions.

(b) MM study of Cl_2–HCHO–O_2 mixtures at total pressures of 930 mbar (700 Torr), with diode laser IR spectroscopy for HO_2 and $HOCH_2O_2$ radicals. The rate coefficient k was obtained from a computer simulation of HO_2 absorption profiles based on a mechanism of eight elementary reactions.

(c) Same experimental system as for comment (b). The branching ratio was determined from a computer simulation of the quantum yields of HCOOH formation.

(d) See Comments on Preferred Values.

Preferred Values ($k = k_1 + k_2$)

$k = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.6 \times 10^{-15} \exp(2300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 275–335 K.

$k_2/k = 0.4$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 1500$ K.
$\Delta(k_1/k) = \pm 0.4$ at 298 K.

Comments on Preferred Values

The two studies[1,2] of the rate coefficient at 298 K are in good agreement and confirm that this reaction is fast compared with the HO_2 radical reactions with CH_3O_2 and $C_2H_5O_2$ radicals. The product channel yielding HCOOH is presumed to proceed via a six-membered cyclic intermediate, analogous to that proposed for the formation of HCHO, CH_3OH, and O_2 from the interaction of CH_3O_2 radicals.[4] Both the temperature dependence and the branching ratio require independent confirmation. In addition, there is the possibility that the rate coefficient could be both pressure and bath-gas dependent. The preferred values are identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K. Moortgat, J. Phys. Chem. **93**, 2368 (1989).
[2] J. P. Burrows, G. K. Moortgat, G. S. Tyndall, R. A. Cox, M. E. Jenkin, G. D. Hayman, and B. Veyret, J. Phys. Chem. **93**, 2375 (1989).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).
[4] M. E. Jenkin, R. A. Cox, G. D. Hayman, and L. J. Whyte, J. Chem. Soc. Faraday Trans. 2 **84**, 913 (1988).

$HO_2 + C_2H_5O_2 \rightarrow O_2 + C_2H_5OOH$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.3\pm0.9)\times10^{-12}$	295	Cattell *et al.*, 1986[1]	MM-IR-AS (a)
$5.6\times10^{-13}\exp[(650\pm125)/T]$	248–380	Dagaut, Wallington, and Kurylo, 1988[2]	FP-AS (b)
$(5.3\pm1.0)\times10^{-12}$	298		
$1.6\times10^{-13}\exp[(1260\pm130)/T]$	248–480	Fenter *et al.*, 1993[3]	FP-AS (c)
$(1.10\pm0.21)\times10^{-11}$	298		
$6.9\times10^{-13}\exp[(702\pm69)/T]$	210–363	Maricq and Szente, 1994[4]	FP-AS (d)
$(8.3\pm1.5)\times10^{-12}$	295		
Reviews and Evaluations			
$5.6\times10^{-13}\exp(650/T)$	250–380	Wallington, Dagaut, and Kurylo, 1992[5]	(e)
$6.5\times10^{-13}\exp(650/T)$	250–380	Lightfoot *et al.*, 1992[6]	(f)
$7.5\times10^{-13}\exp(700/T)$	210–480	NASA, 1997[7]	(g)
$2.7\times10^{-13}\exp(1000/T)$	200–500	IUPAC, 1997[8]	(h)

Comments

(a) MM spectrometry system with HO_2 and $C_2H_5O_2$ radicals generated simultaneously by photolysis of Cl_2 in the presence of C_2H_6–CH_3OH–O_2–N_2 mixtures at pressures of 3.2 mbar (2.4 Torr). HO_2 radicals were monitored by IR absorption with a tunable diode laser and $C_2H_5O_2$ radicals were monitored by UV absorption at 260 nm. The rate coefficient k was determined from the observed perturbation of the second-order kinetics of the HO_2 self-reaction when $C_2H_5O_2$ was present in large excess, and shown to be essentially independent of pressure over the range 3.2–1000 mbar (2.4–760 Torr).

(b) Flash photolysis of Cl_2 in the presence of C_2H_6–CH_3OH–O_2–N_2 mixtures at total pressures of 33–530 mbar (25–400 Torr). Composite transient absorption decay curves for HO_2 and $C_2H_5O_2$ radicals were measured at 230, 250, and 280 nm. Kinetic analysis derived from computer modeling of experimental data.

(c) FP-UV absorption study of Cl_2–C_2H_6–O_2–N_2 mixtures at 1 bar (760 Torr) total pressure. Rate coefficients were derived from simultaneous computer analyses of several decay curves collected at different wavelengths.

(d) FP-UV absorption study of F_2–H_2–C_2H_6–O_2–N_2 mixtures at a total pressure of ~260 mbar (~200 Torr). Rate coefficients were derived from computer simulation of time-resolved decay curves.

(e) Based on the data of Dagaut *et al.*[2]

(f) The rate coefficient of $k=5.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K was derived from the data of Cattell *et al.*[1] and Dagaut *et al.*[2] together with $E/R=-650$ K from Dagaut *et al.*[2]

(g) k_{298} is the weighted average of the data of Cattell *et al.*,[1] Dagaut *et al.*,[2] Fenter *et al.*,[3] and Maricq and Szente,[4] and the E/R is from the data of Dagaut *et al.*,[2] Fenter *et al.*,[3] and Maricq and Szente.[4]

(h) See Comments on Preferred Values.

Preferred Values

$k=7.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=3.8\times10^{-13}\exp(900/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–500 K.

Reliability

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

$\Delta(E/R)=\pm400$ K.

Comments on Preferred Values

The room temperature rate coefficients of Fenter *et al.*[3] and Maricq and Szente[4] are in reasonable agreement with the previous direct studies of Cattell *et al.*[1] and Dagaut *et al.*[2] We have based our recommendations on the average value of k_{298} from these four studies.[1-4] However, the temperature coefficient of Fenter *et al.*[3] is almost a factor of two higher than those of Dagaut *et al.*[2] and Maricq and Szente,[4] indicating a systematic error in one or more of the studies. The rate coefficient determined in all of these studies depend upon the values of $\sigma(HO_2)$ and $\sigma(C_2H_5O_2)$, the latter of which is not well established. Clearly more work is needed on this reaction and in the meantime we recommend an E/R value corresponding to the rounded-off mean of the three determinations,[2-4] with relatively large error limits.

As discussed in our previous evaluation,[8] the FTIR spectroscopic product study of Wallington and Japar[9] has shown that this reaction has only one channel, to yield $C_2H_5OOH+O_2$.

References

[1] F. C. Cattell, J. Cavanagh, R. A. Cox, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. 2 **82**, 1999 (1986).
[2] P. Dagaut, T. J. Wallington, and M. J. Kurylo, J. Phys. Chem. **92**, 3836 (1988).
[3] F. F. Fenter, V. Catoire, R. Lesclaux, and P. D. Lightfoot, J. Phys. Chem. **97**, 3530 (1993).
[4] M. M. Maricq and J. J. Szente, J. Phys. Chem. **98**, 2078 (1994).
[5] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).
[6] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).
[7] NASA Evaluation No. 12, 1997 (see references in Introduction).
[8] IUPAC, Supplement V, 1997 (see references in Introduction).
[9] T. J. Wallington, and S. M. Japar, Chem. Phys. Lett. **166**, 495 (1990).

$$HO_2 + CH_3C(O)O_2 \rightarrow O_2 + CH_3C(O)OOH \quad (1)$$

$$\rightarrow O_3 + CH_3C(O)OH \quad (2)$$

$\Delta H^\circ(2) = -132\ \mathrm{kJ \cdot mol^{-1}}$

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

$k/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.3 \times 10^{-13} \exp[(1040 \pm 100)/T]$	253–368	Moortgat, Veyret, and Lesclaux, 1989[1]	FP-AS (a)
$(1.3 \pm 0.3) \times 10^{-11}$	298		
Branching Ratios			
$k_2/k = 0.25$	298	Niki *et al.*, 1985[2]	FTIR (b)
$k_2/k = 0.33 \pm 0.07$	253–368	Moortgat, Veyret, and Lesclaux, 1989[1]	FP-AS (c)
$k_2/k = 8.5 \times 10^{-3} \exp(1020/T)$	263–333	Horie and Moortgat, 1992[3]	FTIR (d)
$k_2/k = 0.26$	298		
Reviews and Evaluations			
$4.3 \times 10^{-13} \exp(1040/T)$	253–368	Wallington, Dagaut, and Kurylo, 1992[4]	(c)
$k_2/k = 0.33$	253–300		(e)
$4.3 \times 10^{-13} \exp(1040/T)$	253–368	Lightfoot *et al.*, 1992[5]	(e)
$k_2/k = 0.33$	253–368		(e)
$4.5 \times 10^{-13} \exp(1000/T)$	253–368	NASA, 1997[6]	(e)
$4.3 \times 10^{-13} \exp(1040/T)$	250–370	IUPAC, 1997[7]	(f)
$k_2/k = 8.5 \times 10^{-3} \exp(1020/T)$	260–340		(f)

Comments

(a) Flash photolysis of Cl_2 in the presence of $CH_3CHO–CH_3OH–O_2–N_2$ mixtures at total pressures of 800–860 mbar (600–650 Torr). $[CH_3CO_3]$ was monitored by UV absorption over the wavelength range 195–280 nm and the absorption cross section measured relative to $\sigma(HO_2) = 5.3 \times 10^{-18}\ \mathrm{cm^2\ molecule^{-1}}$ at 210 nm. Rate coefficients were derived from a computer simulation of absorption traces at a range of wavelengths, based on a mechanism including secondary removal of CH_3CO_3.

(b) FTIR study of irradiated $Cl_2–HCHO–CH_3CHO–O_2$ mixtures. The branching ratio was based on the analysis of the products $CH_3C(O)OOH$, $CH_3C(O)OH$, and O_3.

(c) Derived from the same experiments as in comment (a) by making allowance for absorption by O_3 product.

(d) FTIR study of irradiated $CH_3C(O)C(O)CH_3$ in the presence of $Ar–O_2$ mixtures at total pressures of 970–1020 mbar (730–770 Torr). The reaction products CO_2, CO, HCHO, HCOOH, $CH_3C(O)OH$, $CH_3C(O)OOH$, CH_3OH, H_2O_2, and O_3 were analyzed by matrix-isolation FTIR spectroscopy combined with a molecular-beam sampling technique. The branching ratio obtained was $\ln(k_1/k_2) = \{(5.8 \pm 1.7) - [(1430 \pm 480)/T]\}$, derived from the yields of $CH_3C(O)OH$ and O_3.

(e) Based on the data of Moortgat *et al.*[1]

(f) See Comments on Preferred Values.

Preferred Values

$k = 1.4 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K.

$k = 4.3 \times 10^{-13} \exp(1040/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ over the temperature range 250–370 K.

$k_2/k = 0.26$ at 298 K.

$k_2/k = 8.5 \times 10^{-3} \exp(1020/T)$ over the temperature range 260–340 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.
$\Delta(E_2/R - E/R) = \pm 500$ K.

Comments on Preferred Values

The recommended value of k together with its temperature dependence are unaltered since our last evaluation,[7] and are based on the data of Moortgat *et al.*[1] Independent confirmation is required to lower the error limits. The study of the products of the reaction by Horie and Moortgat,[3] leading to the measurement of the branching ratio, is much more direct than the previous study of Moortgat *et al.*[1] and, in contrast to the results of Moortgat *et al.*,[1] show a marked temperature dependence. The data of Horie and Moortgat[3] for the branching ratios are recommended, and are in reasonable agreement with the room temperature measurements of the branching ratio made by Niki *et al.*[2]

[1] G. K. Moortgat, B. Veyret, and R. Lesclaux, Chem. Phys. Lett. **160**, 443 (1989).
[2] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **89**, 588 (1985).
[3] O. Horie and G. K. Moortgat, J. Chem. Soc. Faraday Trans. **88**, 3305 (1992).
[4] T. J. Wallington, P. Dagaut, and M. J. Kurylo, Chem. Rev. **92**, 667 (1992).
[5] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).
[6] NASA Evaluation No. 12, 1997 (see references in Introduction).
[7] IUPAC, Supplement V, 1997 (see references in Introduction).

$HO_2 + HOCH_2CH_2O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.8\pm1.5)\times10^{-12}$	298	Jenkin and Cox, 1991[1]	MM-AS (a)
$\sim2.0\times10^{-11}$	298	Anastasi *et al.*, 1991[2]	PR-AS (b)
$(1.2\pm0.3)\times10^{-11}$	296	Murrells *et al.*, 1991[3]	PLP-AS (c)
Reviews and Evaluations			
1.0×10^{-11}	298	IUPAC, 1997[4]	(d)

Comments

(a) MM study with $HOCH_2CH_2O_2$ radicals being generated from the photolysis of $HOCH_2CH_2O_2I$ in the presence of O_2 and N_2 at total pressures of 13, 130, and 1000 mbar (10, 100, and 760 Torr) in a slow flow system. The modulated absorption spectrum in the range 205–310 nm showed that additional transient species were absorbing, and these were ascribed to $HOCH_2CH_2OOI$ and HO_2. The rate coefficient was obtained from computer simulations of the time-resolved absorption waveforms at 220–310 nm for experiments at 13 mbar (10 Torr) pressure.

(b) Pulse radiolysis study, with $HOCH_2CH_2O_2$ radicals being generated from CH_4–O_2–H_2O–SF_6 and CH_3CH_2OH–O_2–SF_6 mixtures at total pressures of 1 bar (760 Torr). $[HOCH_2CH_2O_2]$ was monitored by absorption at 230 nm and k derived from kinetic modeling of absorption profiles.

(c) Pulsed laser photolysis study, with $HOCH_2CH_2O_2$ radicals being generated from photolysis of $HOCH_2CH_2Cl$ in the presence of O_2 and N_2 at total pressures of 970 mbar (730 Torr). The rate coefficient was obtained by modeling the observed absorption profiles on the basis of a simplified mechanism of four reactions.

(d) See Comments on Preferred Values.

Preferred Values

$k = 1.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The pulsed laser photolysis study of Murrells *et al.*[3] of the absorption spectrum of the $HOCH_2CH_2O_2$ radical has shown that the absorption cross-sections reported earlier by Jenkin and Cox[1] from molecular modulation studies of the photolysis of $HOCH_2CH_2I$ are low by a factor of approximately 2. Jenkin and Cox[1] made the assumption that the photolysis of $HOCH_2CH_2I$ in their system yielded entirely $HOCH_2CH_2O_2$ radicals, which was apparently not the case. Increasing $\sigma_{230}(HOCH_2CH_2O_2)$ by a factor of 2 in the re-interpretation[3] of the data of Jenkin and Cox[1] yields a revised value of $k = (8.4\pm3.0)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

The recommended rate coefficient is the mean of this revised value together with the value of Murrells *et al.*[3] The approximate value derived by Anastasi *et al.*[2] from pulse radiolysis experiments is a factor of two higher than our recommended value, and we have not taken this value of Anastasi *et al.*[2] into account, owing to the differences in the absorption spectrum of the radical observed by Anastasi *et al.*[2] compared with the consistent spectra reported by Jenkin and Cox[1] and Murrells *et al.*[3] (see the data sheet for the reaction 2 $HOCH_2CH_2O_2 \rightarrow$ products). The preferred value is identical to that in our previous evaluation.[4]

References

[1] M. E. Jenkin and R. A. Cox, J. Phys. Chem. **95**, 3229 (1991).

[2] C. Anastasi, D. J. Muir, V. J. Simpson, and P. Pagsberg, J. Phys. Chem. **95**, 5791 (1991).

[3] T. P. Murrells, M. E. Jenkin, S. J. Shalliker, and G. D. Hayman, J. Chem. Soc. Faraday Trans. **87**, 2351 (1991).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$$HO_2 + CH_3OCH_2O_2 \rightarrow O_2 + CH_3OCH_2OOH \qquad (1)$$

$$\rightarrow O_2 + CH_3OCHO + H_2O \qquad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Branching Ratios			
$k_1/k = 0.53 \pm 0.08$	295	Wallington *et al.*, 1993[1]	P-FTIR (a)
$k_2/k = 0.40 \pm 0.04$	295		
Reviews and Evaluations			
$k_1/k = 0.60$	298	IUPAC, 1997[2]	(b)
$k_2/k = 0.40$	298		(b)

Comments

(a) HO_2 and $CH_3OCH_2O_2$ radicals were generated from the steady-state photolysis of Cl_2 in the presence of $CH_3OH-CH_3OCH_3-O_2$ mixtures at a total pressure of 930 mbar (700 Torr). Branching ratios were derived from FTIR analyses of CH_3OCHO and CH_3OCH_2OOH products, which accounted for (93±12)% of the CH_3OCH_3 loss.

(b) See Comments on Preferred Values.

Preferred Values

$k_1/k = 0.60$ at 298 K.
$k_2/k = 0.40$ at 298 K.

Reliability

$\Delta(k_1/k) = \pm 0.10$ at 298 K.
$\Delta(k_2/k) = \pm 0.10$ at 298 K.

Comments on Preferred Values

Our recommendations are unaltered since the last IUPAC evaluation.[2] The reaction between HO_2 radicals and $CH_3OCH_2O_2$ radicals is analogous to that between HO_2 radicals and $HOCH_2O_2$ radicals in that there are two channels of nearly equal importance at room temperature, producing: (i) the hydroperoxide plus O_2 and (ii) a carbonyl product, H_2O and O_2. In contrast, the HO_2 reactions with unsubstituted alkyl peroxy radicals, RO_2, appear to have only a single channel, producing the alkyl hydroperoxide.

It has been proposed[1] that the reaction between HO_2 and substituted RO_2 radicals yielding the carbonyl compounds proceeds through a six-member transition state similar to that suggested by Russell[3] to explain the molecular products from the interactions of RO_2 radicals.

References

[1] T. J. Wallington, M. D. Hurley, J. C. Ball, and M. E. Jenkin, Chem. Phys. Lett. **211**, 41 (1993).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

[3] G. Russell, J. Am. Chem. Soc. **79**, 3871 (1957).

$HO_2 + CH_3COCH_2O_2 \rightarrow O_2 + CH_3COCH_2OOH$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.0\pm1.0)\times10^{-12}$	298	Bridier *et al.*, 1993[1]	FP-AS (a)
Reviews and Evaluations			
9.0×10^{-12}	298	IUPAC, 1997[2]	(b)

Comments

(a) Flash photolysis of Cl_2 in the presence of CH_3COCH_3–CH_3OH–N_2 mixtures at a total pressure of 1 bar. The rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 210 and 230 nm.

(b) See Comments on Preferred Values.

Preferred Values

$k = 9.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

Our recommendation is unaltered since the last IUPAC evaluation.[2] While the above value of the rate coefficient seems reasonable, it has been obtained from the kinetic analysis of a complex chemical system and requires independent verification to reduce the recommended error limits. No evidence was obtained by Bridier *et al.*[1] for products other than O_2 and CH_3COCH_2OOH.

References

[1] I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. **89**, 2993 (1993).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$HO_2 + HCHO \rightarrow HOCH_2OO$

$\Delta H° = -68.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.1\pm0.4)\times10^{-13}$	273	Barnes *et al.*, 1985[1]	S-FTIR (a)
7.7×10^{-15} exp[$(625\pm550)/T$]	275–333	Veyret *et al.*, 1989[2]	FP-AS (b)
$(6.0\pm0.7)\times10^{-14}$	295		
Reviews and Evaluations			
6.7×10^{-15} exp($600/T$)	275–333	NASA, 1997[3]	(c)
9.7×10^{-15} exp($625/T$)	275–333	IUPAC, 1997[4]	(d)

Comments

(a) FTIR spectroscopic study in a 420 L reaction chamber. HO_2 radicals were generated from the thermal decomposition of HO_2NO_2 in the presence of HCHO, NO_2, and synthetic air at a total pressure of 530 mbar (400 Torr). The rate coefficient k was obtained from a computer simulation of the rates of decay of HCHO and rates of formation of HCOOH and $HOCH_2O_2NO_2$, based on a reaction scheme consisting of nine elementary reactions.

(b) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2 with long-path absorption measurements of HO_2 and $HOCH_2O_2$ radicals at total pressures of 110–230 mbar (85–170 Torr). The rate coefficient k was obtained from a computer simulation of the absorption profiles based on a mechanism of five elementary reactions.

(c) k_{298} obtained from average of values obtained by Su *et al.*[5] and Veyret *et al.*[2,6] The temperature dependence was taken from Veyret *et al.*[2]

Preferred Values

$k = 7.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.7 \times 10^{-15} \exp(625/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 275–333 K.

Reliability

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

$\Delta(E/R) = \pm 600$ K.

Comments on Preferred Values

Our recommendations are unchanged from the last IUPAC evaluation.[4] The studies of Barnes *et al.*[1] and of Veyret *et al.*[2] are in excellent agreement regarding this rate coefficient, and both are in good agreement with the earlier data of Veyret *et al.*[6] The preferred rate equation is derived by taking an average value of the rate coefficients of Barnes *et al.*[1] [$k(273\text{ K}) = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}] and of Veyre *et al.*[2] [$k(275\text{ K}) = 8.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}] together with the value of E/R determined by Veyret *et al.*[2]

This reaction is believed to proceed via the initial formation of the adduct radical, HO_2CH_2O, which rapidly isomerizes to the product radical, $HOCH_2OO$ via H-atom transfer

References

[1] I. Barnes, K. H. Becker, E. H. Fink, A. Reimer, F. Zabel, and H. Nik Chem. Phys. Lett. **115**, 1 (1985).

[2] B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K Moortgat, J. Phys. Chem. **93**, 2368 (1989).

[3] NASA Evaluation No. 12, 1997 (see references in Introduction).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

[5] F. Su, J. G. Calvert, J. H. Shaw, H. Niki, P. D. Maker, C. M. Savage, an L. P. Breitenbach, Chem. Phys. Lett. **65**, 221 (1979).

[6] B. Veyret, J.-C. Rayez, and R. Lesclaux, J. Phys. Chem. **86**, 3424 (1982)

$HOCH_2OO \rightarrow HO_2 + HCHO$

$\Delta H^\circ = 68.1$ kJ·mol^{-1}

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
20^{+20}_{-10}	273	Barnes *et al.*, 1985[1]	S-FTIR (a)
$2.0 \times 10^{12} \exp[-(7000 \pm 2000)/T]$	275–333	Veyret *et al.*, 1989[2]	FP-AS (b)
100 ± 50	295		
Reviews and Evaluations			
$2.4 \times 10^{12} \exp(-7000/T)$	275–333	IUPAC, 1997[3]	(c)

Comments

(a) FTIR spectroscopic study in a 420 L reaction chamber. HO_2 radicals were generated from the thermal decomposition of HO_2NO_2 in the presence of HCHO, NO_2, and synthetic air at total pressures of 530 mbar (400 Torr). The rate coefficient k was derived from a computer simulation of the rates of decay of HCHO and rates of formation of HCOOH and $HOCH_2O_2NO_2$ based on a reaction scheme consisting of nine elementary reactions.

(b) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2 with long-path absorption measurements of $[HO_2]$ and $[HOCH_2O_2]$ at total pressures of 110–230 mbar (85–170 Torr). The rate coefficient k was obtained from a computer simulation of the absorption profiles based on a mechanism of five elementary reactions.

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.5 \times 10^2$ s^{-1} at 298 K.

$k = 2.4 \times 10^{12} \exp(-7000/T)$ s^{-1} over the temperature range 275–333 K.

Reliability

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

$\Delta(E/R) = \pm 2000$ K.

Comments on Preferred Values

Our recommendations are unchanged from the last IUPAC evaluation.[3] The studies of Barnes *et al.*[1] and of Veyret *et al.*[2] are in good agreement regarding the rate coefficient of this reaction. The preferred rate equation has been obtained by taking the average of the rate coefficients at 273–275 K from these studies together with the E/R determined by Veyret *et al.*[2] It should be pointed out that the equilibrium constant K_1 for the reactions $HO_2 + HCHO \rightleftarrows HOCH_2O_2$ (1,−1), $K_1 = 5.0 \times 10^{-16}$ cm^3 molecule^{-1} at 298 K, derived from the kinetic study of Veyret *et al.*[2] (which is identical to the value obtained from our recommended data for k_1 and k_{-1}) is in excellent agreement with the value of $K_1 = 4.0 \times 10^{-16}$ cm^3 molecule^{-1} at 298 K obtained independently by Burrows *et al.*[4] from molecular modulation studies. The above value of K_1 is, however, considerably smaller than the value of $K_1 = 3.4 \times 10^{-15}$ cm^3 molecule^{-1} at 298 K reported by Zabel *et al.*[5] from electron paramagnetic resonance (EPR) spectroscopic measurements of the ratio of concentrations of HO_2 and $HOCH_2OO$ radicals in the photolysis of $HCHO-O_2$ mixtures.

References

[1] I. Barnes, K. H. Becker, E. H. Fink, A. Reimer, F. Zabel, and H. Niki, Chem. Phys. Lett. **115**, 1 (1985).

[2] B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K. Moortgat, J. Phys. Chem. **93**, 2368 (1989).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

[4] J. P. Burrows, G. K. Moortgat, G. S. Tyndall, R. A. Cox, M. E. Jenkin, G. D. Hayman, and B. Veyret, J. Phys. Chem. **93**, 2375 (1989).

[5] F. Zabel, K. A. Sahetchian, and C. Chachaty, Chem. Phys. Lett. **134**, 433 (1987).

$NO_3 + CH_4 \rightarrow HNO_3 + CH_3$

$\Delta H^\circ = 12.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<4 \times 10^{-16}$	298	Burrows, Tyndall, and Moortgat, 1985[1]	(a)
$\leq 2 \times 10^{-17}$	298±2	Wallington *et al.*, 1986[2]	FP-A (b)
$\leq 8 \times 10^{-19}$	302	Boyd *et al.*, 1991[3]	(c)
Relative Rate Coefficients			
$<6 \times 10^{-21}$	~298	Cantrell *et al.*, 1987[4]	(d)
Reviews and Evaluations			
$<1 \times 10^{-18}$	298	Atkinson, 1997[5]	(e)
$<1 \times 10^{-18}$	298	IUPAC, 1997[6]	(f)

Comments

(a) NO_3 radicals were generated by the modulated photolysis of $Cl_2-ClONO_2-N_2$ or $F_2-HNO_3-N_2$ mixtures and monitored by optical absorption at 662 nm.

(b) NO_3 radicals were generated by the flash photolysis of $ClONO_2-He$ mixtures and detected by optical absorption at 662 nm.

(c) Stopped-flow system with optical absorption detection of NO_3 radicals at 662 nm. The occurrence of secondary reactions was expected to lead to a stoichiometry factor of ≥ 2, resulting in the upper limit to the rate coefficient cited in the table.

(d) Relative rate method. Upper limit to the rate coefficient was derived from the absence of observed CO and CO_2 formation after addition of CH_4 to $N_2O_5-NO_3-NO_2-N_2$ mixtures. An equilibrium constant for the $NO_2 + NO_3 \rightleftarrows N_2O_5$ reactions of 3.41×10^{-11} cm^3 molecule^{-1} at 298 K[7] has been used to derive the rate coefficient cited.

(e) Based on the upper limits derived by Burrows *et al.*,[1] Wallington *et al.*,[2] and Cantrell *et al.*[4]

(f) See Comments on Preferred Values.

Preferred Values

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

Comments on Preferred Values

The preferred value is based on the upper limits to the rate coefficients obtained by Cantrell *et al.*[4] and Boyd *et al.*,[3] and is consistent with the higher upper limits reported by Burrows *et al.*[1] and Wallington *et al.*[2] The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[6]

References

[1] J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, J. Phys. Chem. **89**, 4848 (1985).

[2] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 4640 (1986).

[3] A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, J. Chem. Soc. Faraday Trans. **87**, 2913 (1991).

[4] C. A. Cantrell, J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert, J. Phys. Chem. **91**, 6017 (1987).

[5] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

[7] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

$NO_3 + C_2H_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.9\times10^{-13}\exp[-(2742\pm542)/T]$	295–523	Canosa-Mas *et al.*, 1988[1,2]	DF-A
$(5.1\pm3.5)\times10^{-17}$	295 ± 2		
Relative Rate Coefficients			
$\leq3.0\times10^{-17}$	298 ± 2	Atkinson, Aschmann, and Goodman, 1987[3]	RR (a)
Reviews and Evaluations			
$<1\times10^{-16}$	298	IUPAC, 1997[4]	(b)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5. The concentrations of acetylene and ethene (the reference organic) were measured by GC. The measured rate coefficient ratio of $k(NO_3+C_2H_2)/k(NO_3+C_2H_4)\leq0.14$ at (298 ± 2) K is placed on an absolute basis by use of a rate coefficient of $k(NO_3+C_2H_4)=2.1\times10^{-16}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) See Comments on Preferred Values.

Preferred Values

$k<1\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The measurement of rate coefficients for low reactivity organics is complicated by the possibility of secondary reactions, leading to erroneously high measured rate coefficients. The relative rate measurements of Atkinson *et al.*[3] show C_2H_2 to be significantly less reactive than C_2H_4. The preferred value of the upper limit to the rate coefficient is sufficiently high to be consistent with the data of Canosa-Mas *et al.*[1] Until there are confirmatory data for the reported temperature dependence[2] of this rate coefficient, no temperature dependence is recommended. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[4]

References

[1] C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2 **84**, 247 (1988).

[2] C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2 **84**, 263 (1988).

[3] R. Atkinson, S. M. Aschmann, and M. A. Goodman, Int. J. Chem. Kinet. **19**, 299 (1987).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$NO_3 + C_2H_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$6.29\times10^{-12}\exp[-(3103\pm145)/T]$	295–523	Canosa-Mas *et al.*, 1988[1,2]	DF-A
$(1.85\pm0.24)\times10^{-16}$	295 ± 2		
$(1.7\pm0.5)\times10^{-16}$	300	Biggs *et al.*, 1991;[3] Boyd *et al.*, 1991[4]	(a)
Relative Rate Coefficients			
$(2.16\pm0.20)\times10^{-16}$	296 ± 2	Atkinson, Aschmann, and Pitts, 1988[5]	RR (b)
Reviews and Evaluations			
$4.88\times10^{-18}\,T^2\exp(-2282/T)$	295–523	Atkinson, 1997[6]	(c)
$3.3\times10^{-12}\exp(-2880/T)$	270–340	IUPAC, 1997[7]	(d)

Comments

(a) Stopped-flow technique with optical absorption of the NO_3 radical at 662 nm. The influence of the reaction $NO_2+NO_3+He \rightarrow N_2O_5+He$ was taken into account by numerical modeling, leading to a stoichiometry factor for NO_3 radical decays of ~1.9 and the cited rate coefficient for the elementary NO_3+ethene reaction.

(b) NO_3 radicals were generated by the thermal decomposition of N_2O_5. A series of rate coefficient ratios were measured, with the concentrations of the organic compounds involved being measured by GC. Based on rate coefficient ratios for the sets of organic compounds ethene versus 2,3-dimethylbutane, 2,3-dimethylbutane versus tetrahydrofuran, tetrahydrofuran versus propene, propene versus thiophene, thiophene versus bicyclo[2.2.2]-2-octene, and bicyclo[2.2.2]-2-octene versus *trans*-2-butene, a rate coefficient ratio of $k(NO_3+\text{ethene})/k(NO_3+\textit{trans}\text{-2-butene})=0.000554 \pm 0.000050$ was obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(NO_3+\textit{trans}\text{-2-butene})=3.89\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 296 K.[6,8]

(c) Derived from the absolute rate coefficients of Canosa-Mas *et al.*[1,2] and the relative rate coefficient of Atkinson *et al.*,[5] using the three parameter expression $k=CT^2\exp(-D/T)$.

(d) See Comments on Preferred Values.

Preferred Values

$k=2.1\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=3.3\times10^{-12}\exp(-2880/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.

Reliability

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

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

Comments on Preferred Values

The preferred rate coefficient is derived using the absolute rate coefficient data of Canosa-Mas *et al.*[1,2] and the relative rate coefficient of Atkinson *et al.*[5] These data were fitted to the three parameter expression $k=CT^2\exp(-D/T)$, resulting in $k=4.88\times10^{-18}T^2\exp(-2282/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 295–523 K. The preferred Arrhenius expression, $k=A\exp(-B/T)$, is centered at 300 K and is derived from the three parameter expression with $A=Ce^2T^2$ and $B=D+2T$.

The preferred rate coefficient is in agreement with the 300 K rate coefficient of Biggs *et al.*[3] and Boyd *et al.*,[4] and the preferred values are identical to those in our previous evaluation, IUPAC, 1997.[7]

References

[1] C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2 **84**, 247 (1988).
[2] C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2 **84**, 263 (1988).
[3] P. Biggs, A. A. Boyd, C. E. Canosa-Mas, D. M. Joseph, and R. P. Wayne, Meas. Sci. Technol. **2**, 675 (1991).
[4] A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, J. Chem. Soc. Faraday Trans. **87**, 2913 (1991).
[5] R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., J. Phys. Chem. **92**, 3454 (1988).
[6] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).
[7] IUPAC, Supplement V, 1997 (see reference in Introduction).
[8] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

$NO_3 + C_2H_6 \rightarrow HNO_3 + C_2H_5$

$\Delta H° = -3.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 4\times10^{-18}$	298±2	Wallington *et al.*, 1986[1]	FP-A (a)
$5.7\times10^{-12}\exp[-(4426\pm337)/T]$	453–553	Bagley *et al.*, 1990[2]	DF-A
2.0×10^{-18}	298*		
$\leq(2.7\pm0.2)\times10^{-17}$	302	Boyd *et al.*, 1991[3]	(b)
Reviews and Evaluations			
1.4×10^{-18}	298	Atkinson, 1997[4]	(c)
$<1\times10^{-17}$	298	IUPAC, 1997[5]	(d)

Comments

(a) NO_3 radicals were generated by the flash photolysis of $ClONO_2$–He mixtures and detected by optical absorption at 662 nm.

(b) Stopped-flow system with optical absorption detection of the NO_3 radical at 662 nm. Secondary reactions were expected to lead to a stoichiometry factor of $\geqslant 2$, leading to the upper limit to the rate coefficient cited in the table.

(c) Estimate based on a group rate coefficient for H-atom abstraction from a $-CH_3$ group of 7×10^{-19} cm^3 molecule^{-1} s^{-1} at 298 K.[6]

(d) See Comments on Preferred Values.

Preferred Values

$k<1\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

Extrapolation of the absolute rate coefficients obtained by Bagley *et al.*[2] over the temperature range 453–553 K to 298 K leads to a 298 K rate coefficient of 2×10^{-18} cm^3 molecule^{-1} s^{-1}, probably uncertain to at least a factor of 2 due to the long extrapolation and possible non-Arrhenius behavior of the rate coefficient for this reaction. The preferred upper limit is based on the upper limit of Wallington *et al.*[1] and extrapolation to 298 K of the elevated temperature rate coefficients of Bagley *et al.*,[2] and is identical to that in our previous evaluation, IUPAC, 1997.[5]

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 4640 (1986).

[2] J. A. Bagley, C. Canosa-Mas, M. R. Little, A. D. Parr, S. J. Smith, S. J. Waygood, and R. P. Wayne, J. Chem. Soc. Faraday Trans. **86**, 2109 (1990).

[3] A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, J. Chem. Soc. Faraday Trans. **87**, 2913 (1991).

[4] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

[6] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

$NO_3 + C_3H_6 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.74\times10^{-13}\exp[-(1171\pm66)/T]$	298–423	Canosa-Mas *et al.*, 1991[1]	DF-A
$(9.3\pm1.2)\times10^{-15}$	298		
Relative Rate Coefficients			
$(6.4\pm1.6)\times10^{-15}$	300	Morris and Niki, 1974[2]	RR (a)
$(1.08\pm0.07)\times10^{-14}$	300	Japar and Niki, 1975[3]	RR (a)
$(7.57\pm1.54)\times10^{-15}$	298±1	Atkinson *et al.*, 1984[4]	RR (a)
$(7.41\pm1.95)\times10^{-15}$	298±1	Atkinson *et al.*, 1984[4]	RR (b)
$(9.45\pm0.47)\times10^{-15}$	296±2	Atkinson, Aschmann, and Pitts, 1988[5]	RR (c)
Reviews and Evaluations			
$4.59\times10^{-13}\exp(-1156/T)$	296–423	Atkinson, 1997[6]	(d)
$4.6\times10^{-13}\exp(-1155/T)$	290–430	IUPAC, 1997[7]	(e)

Comments

(a) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The experimental data were relative to the equilibrium coefficient K for the $NO_3+NO_2\rightleftarrows N_2O_5$ reactions, and are placed on an absolute basis by use of $K=1.26\times10^{-27}\exp(11275/T)$ cm^3 molecule^{-1}.[8]

(b) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The concentrations of propene and trans-2-butene were measured by GC, and a rate coefficient ratio of $k(NO_3+\text{propene})/k(NO_3+\textit{trans}\text{-2-butene})=0.019\pm0.005$ obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(NO_3+\textit{trans}\text{-2-butene})=3.90\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.[6,8]

(c) NO_3 radicals were generated by the thermal decomposition of N_2O_5. A series of rate coefficient ratios were measured, with the concentrations of the organic compounds involved being measured by GC. Based on rate coefficient ratios for the sets of organic compounds, propene versus thiophene, thiophene versus bicyclo[2.2.2]-2-octene, and bicyclo[2.2.2]-2-octene versus *trans*-2-butene, a rate coefficient ratio of $k(NO_3+\text{propene})/k(NO_3+\textit{trans}\text{-2-butene})$

$= 0.0243 \pm 0.0012$ at 296 ± 2 K was obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + trans\text{-}2\text{-butene}) = 3.89 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 296 K.[6,8]

(d) Derived using the room temperature relative rate coefficient of Atkinson *et al.*[5] and the absolute 298–423 K rate coefficients of Canosa-Mas *et al.*[1] These rate coefficients[1,5] were fitted to the Arrhenius expression.

(e) See Comments on Preferred Values.

Preferred Values

$k = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.6 \times 10^{-13} \exp(-1155/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–430 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are derived using the room temperature relative rate coefficient of Atkinson *et al.*[5] and the 298–423 K absolute rate coefficients of Canosa-Mas *et al.*[1] The preferred 298 K rate coefficient is in agreement with the relative rate measurements of Morris and Niki,[2] Japar and Niki,[3] and Atkinson *et al.*[4] when the differing values of the equilibrium constant used for the $N_2O_5 \rightleftarrows NO_3 + NO_2$ reactions are taken into account. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[7]

The NO_3 radical reaction with propene proceeds by initial addition, leading to the formation under simulated tropospheric conditions of HCHO, CH_3CHO, and $CH_3C(O)CH_2ONO_2$.[6,8–12]

References

[1] C. E. Canosa-Mas, S. J. Smith, S. J. Waygood, and R. P. Wayne, J. Chem. Soc. Faraday Trans. **87**, 3473 (1991).

[2] E. D. Morris, Jr. and H. Niki, J. Phys. Chem. **78**, 1337 (1974).

[3] S. M. Japar and H. Niki, J. Phys. Chem. **79**, 1629 (1975).

[4] R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **88**, 1210 (1984).

[5] R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., J. Phys. Chem. **92**, 3454 (1988).

[6] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

[7] IUPAC, Supplement V, 1997 (see references in Introduction).

[8] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

[9] H. Bandow, M. Okuda, and H. Akimoto, J. Phys. Chem. **84**, 3604 (1980).

[10] P. B. Shepson, E. O. Edney, T. E. Kleindienst, J. H. Pittman, G. R. Namie, and L. T. Cupitt, Environ. Sci. Technol. **19**, 849 (1985).

[11] I. Barnes, V. Bastian, K. H. Becker, and Z. Tong, J. Phys. Chem. **94**, 2413 (1990).

[12] J. Hjorth, C. Lohse, C. J. Nielsen, H. Skov, and G. Restelli, J. Phys. Chem. **94**, 7494 (1990).

$$NO_3 + C_3H_8 \rightarrow HNO_3 + CH_3CH_2CH_2 \quad (1)$$

$$\rightarrow HNO_3 + CH_3CHCH_3 \quad (2)$$

$\Delta H°(1) = -6.8$ kJ·mol^{-1}

$\Delta H°(2) = -14.3$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq (4.8 \pm 1.7) \times 10^{-17}$	298	Boyd *et al.*, 1991[1]	(a)
Reviews and Evaluations			
1.7×10^{-17}	298	Atkinson, 1997[2]	(b)
$< 7 \times 10^{-17}$	298	IUPAC, 1997[3]	(c)

Comments

(a) Stopped-flow system with optical absorption detection of the NO_3 radical at 662 nm. The occurrence of secondary reactions is expected to lead to a stoichiometry factor of ≥ 2, resulting in the upper limit to the rate coefficient cited in the table.

(b) Estimate based on assumed group rate constants for H-atom abstraction from $-CH_3$ and $-CH_2-$ groups.[4]

(c) See Comments on Preferred Values.

Preferred Values

$k < 7 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the upper limit derived by Boyd *et al.*,[1] and is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, J. Chem. Soc. Faraday Trans. **87**, 2913 (1991).

[2] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

[4] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

$NO_3 + n\text{-}C_4H_{10} \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 2\times10^{-17}$	298±2	Wallington *et al.*, 1986[1]	FP-A (a)
$(4.5\pm0.6)\times10^{-17}$	298	Bagley *et al.*, 1990[2]	DF-A
$(1.44\pm0.12)\times10^{-16}$	333		
$(4.6\pm1.2)\times10^{-16}$	373		
$(1.12\pm0.12)\times10^{-15}$	423		
$(3.2\pm0.3)\times10^{-15}$	473		
$(9.0\pm0.4)\times10^{-15}$	523		
Relative Rate Coefficients			
$(6.6\pm1.7)\times10^{-17}$	296±2	Atkinson *et al.*, 1984[3]	RR (b)
Reviews and Evaluations			
$2.76\times10^{-12}\exp(-3279/T)$	298–423	Atkinson, 1994[4], 1997[5]	(c)

Comments

(a) NO_3 radicals were generated by the flash photolysis of $ClONO_2$ at wavelengths $\gtrsim$180 nm.

(b) NO_3 radicals were produced by the thermal decomposition of N_2O_5, and the concentrations of *n*-butane and *n*-heptane (the reference organic) were measured by GC. A rate constant ratio of $k(NO_3+n\text{-butane})/k(NO_3+n\text{-heptane})=0.48\pm0.12$ was obtained and is placed on an absolute basis by use of a rate coefficient $k(NO_3+n\text{-heptane})=1.37\times10^{-16}$ cm^3 molecule^{-1} s^{-1}.[6]

(c) Based on a least-squares analysis of the 298–423 K absolute rate coefficients of Bagley *et al.*[2]

Preferred Values

$k=4.6\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=2.8\times10^{-12}\exp(-3280/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–430 K.

Reliability

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

$\Delta \log(E/R)=400$ K.

Comments on Preferred Values

The preferred values are based on the absolute rate coefficients measured by Bagley *et al.*[2] over the temperature range 298–423 K (at temperatures >423 K the Arrhenius plot exhibits upward curvature, especially above 473 K). A least-squares analysis of the 298–423 K rate coefficients of Bagley *et al.*[2] results in the preferred Arrhenius expression. The 298 K preferred rate coefficient is a factor of $\gtrsim$2 higher than the upper limit reported by Wallington *et al.*,[1] but is in agreement within the measurement uncertainties with the relative rate coefficient of Atkinson *et al.*[3] At room temperature and below the reaction proceeds mainly by H-atom abstraction from the $-CH_2-$ groups.[2,6]

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 4640 (1986).

[2] J. A. Bagley, C. Canosa-Mas, M. R. Little, A. D. Parr, S. J. Smith, S. J. Waygood, and R. P. Wayne, J. Chem. Soc. Faraday Trans. **86**, 2109 (1990).

[3] R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **88**, 2361 (1984).

[4] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 2**, 1 (1994).

[5] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

[6] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

$NO_3 + HCHO \rightarrow HNO_3 + HCO$

$\Delta H° = -57.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
5.6×10^{-16}	298±2	Cantrell *et al.*, 1985[1]	(a)
Relative Rate Coefficients			
$(5.89 \pm 0.48) \times 10^{-16}$	298±1	Atkinson *et al.*, 1984[2]	(b,c)
$(8.7 \pm 0.6) \times 10^{-16}$	298±2	Cantrell *et al.*, 1985[1]	(c,d)
$(7.9 \pm 1.7) \times 10^{-16}$	295±2	Hjorth, Ottobrini, and Restelli, 1988[3]	(b,c,d)
Reviews and Evaluations			
5.8×10^{-16}	298	NASA, 1997[4]	(e)
5.8×10^{-16}	298	IUPAC, 1997[5]	(f)

Comments

(a) NO_3 radicals were generated *in situ* from the reaction $NO_2 + O_3 \rightarrow NO_3 + O_2$. NO_3 radical concentrations were measured by differential optical absorption spectroscopy (DOAS), and the rate coefficient derived from the measured concentrations of reactants and products by FTIR absorption spectroscopy and DOAS (for the NO_3 radical and NO_2).

(b) NO_3 radicals were generated by the thermal decomposition of N_2O_5.

(c) Relative to the equilibrium coefficient K for the reactions $NO_2 + NO_3 \rightleftarrows N_2O_5$. The experimental data are placed on an absolute basis by use of an equilibrium coefficient of $K = 1.26 \times 10^{-27} \exp(11275/T)$ cm^3 molecule^{-1}.[6]

(d) NO_3 radicals were generated *in situ* from the reaction $NO_2 + O_3 \rightarrow NO_3 + O_2$.

(e) Derived from the data of Atkinson *et al.*,[2] Cantrell *et al.*,[1] and Hjorth *et al.*[3]

(f) See Comments on Preferred Values.

Preferred Values

$k = 5.8 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The data of Atkinson *et al.*,[2] Cantrell *et al.*,[1] and Hjorth *et al.*[3] disagree by a factor of ~1.5 when the same equilibrium constant for the $NO_2 + NO_3 \rightleftarrows N_2O_5$ reactions is used to place the rate coefficients on an absolute basis. However, the rate coefficient obtained by Cantrell *et al.*[1] from experiments which were independent of this equilibrium constant agrees well with that derived from the Atkinson *et al.*[2] data.

Accordingly, a rate coefficient of 5.8×10^{-16} cm^3 molecule^{-1} s^{-1} is recommended, with the uncertainty limits reflecting the need for an absolute measurement. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[5] While no temperature dependence of the rate coefficient has been measured to date, by analogy with the NO_3 radical reaction with CH_3CHO a preexponential factor of $\sim 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is expected, and hence $k(NO_3 + HCHO) \sim 2 \times 10^{-12} \exp(-2430/T)$ cm^3 molecule^{-1} s^{-1}.

This reaction proceeds by H-atom abstraction.

$$NO_3 + HCHO \rightarrow HNO_3 + HCO$$

References

[1] C. A. Cantrell, W. R. Stockwell, L. G. Anderson, K. L. Busarow, D. Perner, A. Schmeltekopf, J. G. Calvert, and H. S. Johnston, J. Phys. Chem. **89**, 139 (1985).

[2] R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **88**, 1210 (1984).

[3] J. Hjorth, G. Ottobrini, and G. Restelli, J. Phys. Chem. **92**, 2669 (1988).

[4] NASA Evaluation No. 12, 1997 (see references in Introduction).

[5] IUPAC Supplement V, 1997 (see references in Introduction).

[6] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

$NO_3 + CH_3CHO \rightarrow HNO_3 + CH_3CO$

$\Delta H° = -53.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.44\times10^{-12}\exp[-(1860\pm300)/T]$	264–374	Dlugokencky and Howard, 1989[1]	F-LIF (a)
$(2.74\pm0.33)\times10^{-15}$	298		
Relative Rate Coefficients			
$(2.54\pm0.64)\times10^{-15}$	300	Morris and Niki, 1974[2]	RR (b)
$(2.44\pm0.52)\times10^{-15}$	298±1	Atkinson *et al.*, 1984[3]	RR (b)
$(3.15\pm0.60)\times10^{-15}$	299±1	Cantrell *et al.*, 1986[4]	RR (b)
Reviews and Evaluations			
$1.4\times10^{-12}\exp(-1900/T)$	260–370	NASA, 1997[5]	(c)
$1.4\times10^{-12}\exp(-1860/T)$	260–370	IUPAC, 1997[6]	(d)

Comments

(a) NO_3 radicals were generated by the thermal dissociation of N_2O_5 in a flow system.

(b) The cited rate coefficients are relative to the equilibrium coefficient K for the reactions $NO_2+NO_3 \rightleftarrows N_2O_5$, with $K=1.26\times10^{-27}\exp(11275/T)$ cm^3 molecule^{-1} being used[7] to place the measured data on an absolute basis.

(c) The 298 K rate coefficient was the average of the values of Atkinson *et al.*,[3] Cantrell *et al.*,[4] and Dlugokencky and Howard,[1] with the temperature dependence being that of Dlugokencky and Howard.[1]

(d) See Comments on Preferred Values.

Preferred Values

$k=2.7\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.4\times10^{-12}\exp(-1860/T)$ cm^3 molecule^{-1}s^{-1} over the temperature range 260–370 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are based upon the sole absolute rate coefficient study of Dlugokencky and Howard.[1] The rate coefficients reported by Morris and Niki,[2] Atkinson *et al.*,[3] and Cantrell *et al.*[4] (when reevaluated[7] to be consistent with recent values of the equilibrium constant for the $NO_2+NO_3 \rightleftarrows N_2O_5$ reactions) are in good agreement with this preferred value. However, because of the significant uncertainties in this equilibrium constant,[7] these relative rate coefficient data were not used in the evaluation of the preferred rate coefficient. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[6]

References

[1] E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **93**, 1091 (1989).

[2] E. D. Morris, Jr. and H. Niki, J. Phys. Chem. **78**, 1337 (1974).

[3] R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **88**, 1210 (1984).

[4] C. A. Cantrell, J. A. Davidson, K. L. Busarow, and J. G. Calvert, J. Geophys. Res. **91**, 5347 (1986).

[5] NASA Evaluation No. 12, 1997 (see references in Introduction).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

[7] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

$NO_3 + CH_3COCH_3 \rightarrow HNO_3 + CH_3COCH_2$

$\Delta H° = -15.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq (8.5 \pm 2.5) \times 10^{-18}$	302	Boyd *et al.*, 1991[1]	(a)
Reviews and Evaluations			
$< 3 \times 10^{-17}$	298	IUPAC, 1997[2]	(b)

Comments

(a) Stopped flow system with detection of the NO_3 radical by optical absorption at 662 nm. Secondary reactions were believed to be important and a stoichiometry factor of ≥ 2 has been used to obtain the cited upper limit to the rate coefficient.

(b) See Comments on Preferred Values.

Preferred Values

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

Comments on Preferred Values

The upper limit to the preferred value is derived from the overall rate coefficient of $(1.7 \pm 0.5) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} measured by Boyd *et al.*,[1] with no account taken of the expected greater than unity stoichiometry. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[2]

References

[1] A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, J. Chem. Soc. Faraday Trans. **87**, 2913 (1991).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$NO_3 + CH_3OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 6 \times 10^{-16}$	298±2	Wallington *et al.*, 1987[1]	FP-A
$1.25 \times 10^{-12} \exp[-(2562 \pm 241)/T]$	294–473	Canosa-Mas *et al.*, 1989[2]	DF-A
$(2.1 \pm 1.1) \times 10^{-16}$	294		
$1.06 \times 10^{-12} \exp[-(2093 \pm 803)/T]$	258–367	Langer and Ljungström, 1995[3]	DF-A (a)
$(1.32 \pm 0.24) \times 10^{-16}$	295		
Reviews and Evaluations			
$1.3 \times 10^{-12} \exp(-2560/T)$	290–480	IUPAC, 1997[4]	(b)

Comments

(a) The cited Arrhenius expression leads to a rate coefficient at 295 K of 8.8×10^{-16} cm^3 molecule^{-1} s^{-1}, clearly in disagreement with the measured value. A unit-weighted least-squares analysis of the rate coefficients measured by Langer and Ljungström[3] (Table 3 of Langer and Ljungström[3]) leads to $k = 9.36 \times 10^{-13} \exp[-(2652 \pm 312)/T]$ cm^3 molecule^{-1} s^{-1}, where the indicated error is one standard deviation.

(b) Based on the absolute rate coefficients of Canosa-Mas *et al.*[2]

Preferred Values

$k = 1.3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.4 \times 10^{-13} \exp(-2650/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.

Reliability

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

$\Delta(E/R) = \pm 700$ K.

Comments on Preferred Values

The reported rate coefficients of Canosa-Mas *et al.*[2] are higher by factors of 1.6–2.1 than those of Langer and Ljungström[3] over the temperature range common to both studies (294–373 K). Clearly there are systematic errors in one or both of these studies. Based on the observation that for the NO_3 radical reaction with 2-propanol the data of Langer and Ljungström[3] may still be an upper limit to the rate coefficient (see data sheet for NO_3+2-propanol), the preferred values were derived from the data of Langer and Ljungström[3] using the Arrhenius parameters given in comment (a). The 298 K rate coefficient is calculated from the resulting Arrhenius expression. It is possible that the preferred values are still high because of the potential for secondary reactions in slowly reacting systems using absolute rate methods.

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., Int. J Chem. Kinet. **19**, 243 (1987).

[2] C. E. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc Faraday Trans. 2 **85**, 709 (1989).

[3] S. Langer and E. Ljungström, J. Chem. Soc. Faraday Trans. **91**, 405 (1995).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$NO_3 + C_2H_5OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 9\times10^{-16}$	298±2	Wallington *et al.*, 1987[1]	FP-A
6.99×10^{-13} exp[$-(1815\pm419)/T$]	273–367	Langer and Ljungström, 1995[2]	DF-A
$(1.81\pm0.26)\times10^{-15}$	297		
Reviews and Evaluations			
$<2\times10^{-15}$	298	IUPAC, 1997[3]	(a)

Comments

(a) Based on the upper limit to the rate coefficient determined by Wallington *et al.*[1]

Preferred Values

$k = <2\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

By analogy with the data for the reaction of the NO_3 radical with 2-propanol (see data sheet in this evaluation), it is likely that the rate coefficients of Langer and Ljungström[2] are high because of the occurrence of secondary reactions. The preferred value is based on the upper limit to the rate coefficient determined by Wallington *et al.*,[1] and is consistent with the 298 K rate coefficient of Langer and Ljungström[2] calculated from their Arrhenius expression. No recommendation is made concerning the temperature dependence. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **19**, 243 (1987).

[2] S. Langer and E. Ljungström, J. Chem. Soc. Faraday Trans. **91**, 405 (1995).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$$NO_3 + CH_3CH(OH)CH_3 \rightarrow HNO_3 + CH_3\dot{C}(OH)CH_3 \quad (1)$$

$$\rightarrow HNO_3 + \dot{C}H_2CH(OH)CH_3 \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 2.3\times10^{-15}$	298±2	Wallington *et al.*, 1987[1]	FP-A
$1.54\times10^{-12}\exp[-(1743\pm1009)/T]$	273–364	Langer and Ljungström, 1995[2]	DF-A
$(3.13\pm0.64)\times10^{-15}$	295		
Relative Rate Coefficients			
$\leq(1.7\pm0.6)\times10^{-15}$	298±2	Chew, Atkinson, and Aschmann, 1998[3]	RR (a)
$k_1=(1.3\pm0.5)\times10^{-15}$	298±2	Chew, Atkinson, and Aschmann, 1998[3]	RR (a)
Reviews and Evaluations			
$<5\times10^{-15}$	298	IUPAC, 1997[4]	(b)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in air at atmospheric pressure. Experiments were carried out in a ~7000 L Teflon chamber, and the concentrations of 2-propanol and methacrolein (the reference organic) were measured by GC. Rate coefficient ratios $k(NO_3+\text{2-propanol})/k(NO_3+\text{methacrolein})$ were measured as a function of initially added NO_2 over the range $(0-2.4)\times10^{14}$ molecule cm^{-3}(~2×10^{16} molecule cm^{-3} of ethane were added when no NO_2 was initially added). The rate coefficient ratios were independent of initial NO_2 concentration in the range $(0-4.8)\times10^{13}$ molecule cm^{-3}, but increased for initial NO_2 concentrations $\geq 9.6\times10^{13}$ molecule cm^{-3}. Acetone was observed as a reaction product, presumably from channel (1) followed by

$$CH_3\dot{C}(OH)CH_3+O_2 \rightarrow CH_3C(O)CH_3+HO_2$$

with a yield of ~0.76 ± 0.09 at initial NO_2 concentrations of $(0-4.8)\times10^{13}$ molecule cm^{-3} decreasing at higher initial NO_2 concentrations. The values of $\{k(NO_3+\text{2-propanol})(\text{yield of acetone})/k(NO_3+\text{methacrolein})\}$ were independent of initial NO_2 concentration over the entire range studied $[(0-2.4)\times10^{14}$ molecule cm$^{-3}]$, with an average value of 0.40 ± 0.06 for experiments with initial NO_2 concentrations of $(0-4.8)\times10^{13}$ molecule cm^{-3}. The observed behavior is interpreted as involving a gas-phase reaction of 2-propanol with the NO_3 radical and a reaction (gas-phase or heterogeneous) of N_2O_5 with 2-propanol to form nitrates.[2] The rate coefficient k is obtained from the rate coefficient ratio $k(NO_3+\text{2-propanol})/k(NO_3+\text{methacrolein})=0.519\pm0.053$ at low added NO_2 concentration, combined with a rate coefficient of $k(NO_3+\text{methacrolein})=(3.3\pm1.0)\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at (298 ± 2) K.[3] This overall rate coefficient could still be an upper limit, and the true rate coefficient may be the value obtained for k_1 obtained from the ratio $\{k(NO_3+\text{2-propanol})(\text{yield of 2-acetone})/k_2(NO_3+\text{methacrolein})=0.40\pm0.06$ and the rate coefficient of $k(NO_3+\text{methacrolein})$.[3]

(b) Based on the upper limit to the rate coefficient of Wallington *et al.*[1]

Preferred Values

$k=1.3\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k=1.0$ at 298 K.

Reliability

$\Delta \log k=\pm0.3$ at 298 K.
$\Delta(k_1/k)=\pm0.3$ at 298 K.

Comments on Preferred Values

The room temperature values for the overall reaction rate coefficient k and for k_1 obtained by Chew *et al.*[3] are consistent with the upper limit to the rate coefficient of Wallington *et al.*,[1] but are a factor of ~2–3 lower than the absolute rate coefficient of Langer and Ljungström.[2] It is expected that the reaction of the NO_3 radical occurs almost entirely by H-atom abstraction from the tertiary C–H bond (and hence that $k_1/k\sim1.0$).[5] This expectation is consistent with the data of Chew *et al.*[3] The 298 K preferred value is based on the value of k_1 obtained by Chew *et al.*[3] with the expectation that $k_1/k=1.0$.[5] No temperature dependence is recommended.

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **19**, 243 (1987).

[2] S. Langer and E. Ljungström, J. Chem. Soc. Faraday Trans. **91**, 405 (1995).

[3] A. A. Chew, R. Atkinson, and S. M. Aschmann, J. Chem. Soc. Faraday Trans. **94**, 1083 (1998).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

[5] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

$$\mathrm{NO_3 + CH_3CH(OH)CH_2CH_3 \rightarrow HNO_3 + CH_3C(OH)CH_2CH_3} \quad (1)$$

$$\mathrm{\rightarrow HNO_3 + CH_2CH(OH)CH_2CH_3} \quad (2)$$

$$\mathrm{\rightarrow HNO_3 + CH_3CH(OH)CHCH_3} \quad (3)$$

$$\mathrm{\rightarrow HNO_3 + CH_3CH(OH)CH_2CH_2} \quad (4)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$k \leqslant (2.5\pm0.8)\times10^{-15}$	298±2	Chew, Atkinson, and Aschmann, 1998[1]	RR (a)
$k_1=(2.0\pm0.7)\times10^{-15}$	298±2	Chew, Atkinson, and Aschmann, 1998[1]	RR (a)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in air at atmospheric pressure. Experiments were carried out in a ~7000 L Teflon chamber, and the concentrations of 2-butanol and methacrolein (the reference organic) were measured by GC. Rate coefficient ratios $k(NO_3+$2-butanol$)/k(NO_3+$methacrolein$)$ were measured as a function of initially added NO_2 over the range $(0-2.4)\times10^{14}$ molecule cm^{-3} ($\sim2\times10^{16}$ molecule cm^{-3} of ethane were added when no NO_2 was initially added). The rate coefficient ratios were independent of initial NO_2 concentration in the range $(0-4.8)\times10^{13}$ molecule cm^{-3}, but increased for initial NO_2 concentrations $\geqslant 9.6\times10^{13}$ molecule cm^{-3}. 2-Butanone was observed as a reaction product, presumably from channel (1) followed by

$$\mathrm{CH_3\dot{C}(OH)CH_2CH_3+O_2 \rightarrow CH_3C(O)CH_2CH_3+HO_2}$$

with a yield of $\sim0.79\pm0.09$ at initial NO_2 concentrations of $(0-4.8)\times10^{13}$ molecule cm^{-3}, and decreasing at higher initial NO_2 concentrations. The values of $\{k(NO_3+$2-butanol$)($yield of 2-butanone$)/k(NO_3+$methacrolein$)\}$ were independent of initial NO_2 concentration over the entire range studied $[(0-2.4)\times10^{14}$ molecule cm$^{-3}]$, with an average value of 0.60 ± 0.07 for experiments with initial NO_2 concentrations of $(0-4.8)\times10^{13}$ molecule cm^{-3}. The observed behavior is interpreted as involving a gas-phase reaction of 2-butanol with the NO_3 radical and a reaction (gas-phase or heterogeneous) of N_2O_5 with 2-butanol to form nitrates.[2] The rate coefficient k is obtained from the rate coefficient ratio $k(NO_3+$2-butanol$)/k(NO_3+$methacrolein$)=0.754\pm0.065$ at low added NO_2 concentration, combined with a rate coefficient of $k(NO_3+$methacrolein$)=(3.3\pm1.0)\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at (298 ± 2)K.[1] This overall rate coefficient could still be an upper limit, and the true-rate coefficient may be the value obtained for k_1 obtained from the ratio $\{k(NO_3+$2-butanol$)($yield of 2-butanone$)/k_2(NO_3+$methacrolein$)=0.60\pm0.07$ and the rate coefficient $k(NO_3+$methacrolein$)$.[1]

Preferred Values

$k=2.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k=1.0$ at 298 K.

Reliability

$\Delta \log k=\pm0.3$ at 298 K.
$\Delta(k_1/k)=\pm0.3$ at 298 K.

Comments on Preferred Values

The preferred values are based on the sole study of Chew *et al.*[1] In view of the magnitude of the rate coefficient compared to that for reaction of the NO_3 radical with *n*-butane (this evaluation), reaction is expected to occur almost totally at the tertiary C–H bond (i.e., $k_1/k=1.0$). The preferred value therefore uses the measured rate coefficient k_1 combined with the expectation that $k_1/k=1.0$.

References

[1] A. A. Chew, R. Atkinson, and S. M. Aschmann, J. Chem. Soc. Faraday Trans. **94**, 1083 (1998).
[2] S. Langer and E. Ljungström, J. Chem. Soc. Faraday Trans. **91**, 405 (1995).

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

$\Delta H° = -136.0$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.6×10^{-31} [N_2]	298	Basco, James, and James, 1972[1]	FP-AS (a)
3.1×10^{-31} [N_2]	298	Parkes, 1977[2]	MM-AS (b)
4.5×10^{-31} [N_2]	296	Selzer and Bayes, 1983[3]	PLP-MS (c)
$(7.0\pm1.0)\times10^{-31}$ [Ar]	298	Cobos *et al.*, 1985[4]	PLP-AS (d)
$(8.0\pm1.0)\times10^{-31}$ [N_2]	298		
$(4.8\pm0.6)\times10^{-31}$ [Ar]	298	Pilling and Smith, 1985[5]	PLP-AS (e)
$(1.0\pm0.3)\times10^{-30}(T/300)^{-3.3}$ [Ar]	334–582	Keiffer, Pilling, and Smith, 1987[6]	PLP-AS (f)
Relative Rate Coefficients			
$6.1\times10^{-33}\exp(1000/T)$ [N_2]	259–339	Washida and Bayes, 1976[7]	DF-MS (g)
1.8×10^{-31} [N_2]	298		
$8.0\times10^{-32}\exp(243/T)$ [Ar]	230–568	Pratt and Wood, 1984[8]	(h)
1.8×10^{-31} [Ar]	298		
$(7.56\pm1.1)\times10^{-31}(T/300)^{-3.64}$ [N_2]	264–370	Kaiser, 1993[9]	(i)
Reviews and Evaluations			
$4.5\times10^{-31}(T/300)^{-3.0}$ [air]	200–300	NASA, 1997[10]	(j)
$1.0\times10^{-30}(T/300)^{-3.3}$ [N_2]	200–300	IUPAC, 1997[11]	(k)

Comments

(a) Pressure range 40–500 mbar. Lindemann–Hinshelwood plot was used for extrapolation to k_0 and k_∞.

(b) Molecular modulation spectroscopy. Pressure range 25–1000 mbar. Lindemann–Hinshelwood extrapolation to k_0 and k_∞.

(c) Pressure varied between 0.6 and 8 mbar.

(d) Pressure of the bath gases N_2, Ar, and O_2 varied between 0.2 mbar and 150 bar. Falloff curves were constructed with $F_c=0.27$, $N=1.47$ and $k_\infty=2.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. The low value of the theoretically modeled F_c leads to a high limiting value of k_0 extracted from the measurements.

(e) Pressures of bath gas Ar varied between 4.2 and 645 mbar. Falloff curves constructed using $F_c=0.57$ (including strong and weak collision contributions).

(f) Measurements in the pressure range 25–790 mbar. Falloff curves constructed with $F_c=0.6$. Various fitting procedures were applied and discussed.

(g) The rate coefficients $k(CH_3+O_2+M\rightarrow CH_3O_2+M)$ plus $k(CH_3+O_2\rightarrow HCHO+HO)$ were measured relative to $k(O+CH_3\rightarrow \text{products})$. Evaluation with $k(O+CH_3)=1.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1}. Extrapolation to k_0.

(h) Discharge-flow system at pressures of 2.6–13 mbar. CH_3 radicals were produced from the $H+C_2H_4$ reaction. Reaction rates were determined from the effect of added O_2 on the radical combination products. Falloff curves were constructed assuming that k_∞ and F_c are independent of temperature.

(i) Mixtures of Cl_2, CH_4, diluent (N_2, Ar, He, or SF_6) were irradiated with a fluorescent lamp. The CH_4 loss and CH_3Cl formation were measured by GC. Data were obtained (for N_2 or O_2) between 3 mbar and 13 bar at 297 K, 25 mbar and 2 bar at 370 K and 50 mbar and 15 bar at 264 K. The data were fitted using $F_c=0.48$ at 264 K, 0.46 at 297 K, and 0.42 at 370 K.

(j) Based on the measurements of Selzer and Bayes.[3]

(k) See Comments on Preferred Values.

Preferred Values

$k_0=1.0\times10^{-30}(T/300)^{-3.3}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

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

$\Delta n=\pm1$.

Comments on Preferred Values

The evaluation uses the results of Refs. 6 and 9, although different values of F_c were employed. The temperature dependence of F_c applied in Ref. 6 does not extend to temperatures below 300 K. The calculated values of F_c used in Ref. 12 are preferred, i.e., $F_c=0.27$ at 300 K. The recommendation of IUPAC, 1997[11] remains unchanged.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.8×10^{-12}	298	Van den Bergh and Callear, 1971[13]	FP-AS (a)
5×10^{-13}	298	Basco, James, and James, 1972[1]	FP-AS (b)
1.2×10^{-12}	298	Parkes, 1977[2]	FP-AS (c)
2.2×10^{-12}	295	Hochanadel *et al.*, 1977[14]	FP-AS (d)
$(2.2\pm0.3)\times10^{-12}(T/300)^{0.94}$	200-400	Cobos *et al.*, 1985[4]	PLP-AS (e)
$(1.05\pm0.12)\times10^{-12}$	298	Pilling and Smith, 1985[5]	PLP-AS (f)
$(1.2\pm0.2)\times10^{-12}(T/300)^{1.2}$	334-582	Keiffer, Pilling, and Smith, 1987[6]	PLF-AS (g)
Relative Rate Coefficients			
1.7×10^{-12}	298	Laufer and Bass, 1975[15]	FP-GC (h)
$(1.31\pm0.1)\times10^{-12}(T/300)^{1.2}$	264-370	Kaiser, 1993[9]	(i)
Reviews and Evaluations			
$1.8\times10^{-12}(T/300)^{-1.7}$	200-300	NASA, 1997[10]	(j)
$1.8\times10^{-12}(T/300)^{1.1}$	200-300	IUPAC, 1997[11]	(k)

Comments

(a) Pressure range 40–400 mbar of C_3H_8. RRKM extrapolation to k_∞.

(b) See comment (a) for k_0.

(c) See comment (b) for k_0.

(d) 12% falloff correction applied using the results of Ref. 1.

(e) See comment (d) for k_0.

(f) See comment (e) for k_0.

(g) See comment (f) for k_0.

(h) Pressure range 66–920 mbar, RRKM extrapolation to k_∞. Rate measured relative to $CH_3+CH_3\rightarrow C_2H_6$ and evaluated with $k(CH_3+CH_3\rightarrow C_2H_6)=9.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} from the same work.

(i) See comment (j) for k_0.

(j) See comment (k) for k_0.

(k) See comment (l) for k_0.

Preferred Values

$k=9.5\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_\infty-1.8\times10^{-12}(T/300)^{1.1}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty=\pm0.3$ over the temperature range 200–300 K.
$\Delta n=\pm1$.

Comments on Preferred Values

The preferred value is an average of earlier results from Refs. 4 and 6 and the more recent determination by Kaiser,[9] and is identical to that in our previous evaluation, IUPAC, 1997.[11]

References

[1] N. Basco, D. G. L. James, and F. C. James, Int. J. Chem. Kinet. **4**, 129 (1972).
[2] D. A. Parkes, Int. J. Chem. Kinet. **9**, 451 (1977).
[3] E. A. Selzer and K. D. Bayes, J. Phys. Chem. **87**, 392 (1983).
[4] C. J. Cobos, H. Hippler, K. Luther, A. R. Ravishankara, and J. Troe, J. Phys. Chem. **89**, 4332 (1985).
[5] M. J. Pilling and M. J. C. Smith, J. Phys. Chem. **89**, 4713 (1985).
[6] M. Keiffer, M. J. Pilling, and M. J. C. Smith, J. Phys. Chem. **91**, 6028 (1987).
[7] N. Washida and K. D. Bayes, Int. J. Chem. Kinet. **8**, 777 (1976).
[8] G. L. Pratt and S. W. Wood, J. Chem. Soc. Faraday Trans. 1 **80**, 3419 (1984).
[9] E. W. Kaiser, J. Phys. Chem. **97**, 11681 (1993).
[10] NASA Evaluation No. 12, 1997 (see references in Introduction).
[11] IUPAC, Supplement V, 1997 (see references in Introduction).
[12] IUPAC, Supplement III, 1989 (see references in Introduction).
[13] H. Van den Bergh and A. B. Callear, Trans. Faraday Soc. **67**, 2017 (1971).
[14] C. J. Hochanadel, J. A. Ghormley, J. W. Boyle, and P. J. Ogren, J. Phys. Chem. **81**, 3 (1977).
[15] A. H. Laufer and A. M. Bass, Int. J. Chem. Kinet. **7**, 639 (1975).

$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$

$\Delta H° = -54.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.1\pm0.5)\times10^{-13}$	295	Plumb and Ryan, 1981[1]	(a)
$<10^{-13}$	1000	Wagner *et al.*, 1990[2]	PLP-MS (b)
Relative Rate Coefficients			
1.9×10^{-14} (130 mbar, air)	298	Kaiser, Lorkovic, and Wallington, 1990[3]	(c)
3.8×10^{-15} (1 bar, air)	298		
9.8×10^{-16} (8 bar, air)	298		
Reviews and Evaluations			
$3.3\times10^{-12}\exp(-2510/T)$	700–2000	Warnatz, 1984[4]	(d)
$1.4\times10^{-12}\exp(-1950/T)$	300–2500	Tsang and Hampson, 1986[5]	(e)
$<2.0\times10^{-14}$	200–300	NASA, 1997[6]	(f)
1.9×10^{-14} (0.133 bar)	298	IUPAC, 1997[7]	(g)
3.8×10^{-15} (1 bar)	298		

Comments

(a) Discharge flow system. C_2H_5 radicals were generated from the reaction $Cl+C_2H_6 \rightarrow HCl+C_2H_5$. C_2H_5 and C_2H_4 were measured directly by MS. The rate coefficient k was determined from the measured yields of C_2H_4. k found to be independent of pressure (0.8–13 mbar).

(b) Experimental and theoretical study of the $C_2H_5+O_2$ reaction. Experiments were carried out in tubular flame reactor. C_2H_5 radicals were formed by laser photolysis of C_2H_5Br or CCl_4–C_2H_6 mixtures. Concentrations of C_2H_5 and C_2H_4 were monitored by photoionization MS.

(c) Study of the yields of C_2H_4 produced relative to the C_2H_6 consumed (GC analysis) in a system in which C_2H_5 radicals were generated from UV irradiation of Cl_2–C_2H_6–O_2–N_2 (or air) mixtures. Up to 8 bar the percentage of C_2H_4 produced, relative to the C_2H_6 consumed, decreased from 12% to 0.02%, following a $p^{(-0.8\pm0.1)}$ pressure dependence in air. The listed pressure-dependent k values are relative to values of $k(C_2H_5+O_2+M \rightarrow C_2H_5O_2+M)$ calculated from the preferred recommended values.[8]

(d) Includes high-temperature data from shock tube and other studies.

(e) Based on data from Ref. 8. Included high-temperature data from shock tube and other studies.

(f) Estimation applicable only for lower atmospheric pressure and temperature conditions.

(g) See Comments on Preferred Values.

Preferred Values

$k = 3.8\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k = 1.9\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K and 0.133 bar of air.

Reliability

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

Comments on Preferred Values

The recommended pressure-dependent values of k_{298} are from the product study of Kaiser *et al.*[3] and are identical to those in our previous evaluation, IUPAC, 1997.[7] Increasing the pressure, therefore, decreases the apparent rate coefficient of this reaction. At a given pressure, increasing the temperature leads to an increasing yield of C_2H_4.

For a full discussion on the mechanism of the $C_2H_5+O_2$ reaction see the paper of Wagner *et al.*[2] It is clear that for atmospheric conditions the interaction of C_2H_5 with O_2 to form $C_2H_5O_2$ radicals is by far the dominant pathway. The work of Kaiser[9] provides information on the mechanism of C_2H_4 formation. According to this, the reaction proceeds via a rearrangement of the excited $C_2H_5O_2$ adduct with an energy barrier of (4.6 ± 1.0) kJ mol^{-1}.

References

[1] I. C. Plumb and K. R. Ryan, Int. J. Chem. Kinet. **13**, 1011 (1981).
[2] A. F. Wagner, I. R. Slagle, D. Sarzynski, and D. Gutman, J. Phys. Chem. **94**, 1853 (1990).
[3] E. W. Kaiser, I. M. Lorkovic, and T. J. Wallington, J. Phys. Chem. **94**, 3352 (1990).
[4] J. Warnatz, in *Combustion Chemistry*, edited by W. C. Gardiner (Springer, New York, 1984), p. 197.
[5] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).
[6] NASA Evaluation No. 12, 1997 (see references in Introduction).
[7] IUPAC, Supplement V, 1997 (see references in Introduction).
[8] R. R. Baldwin, I. A. Pickering, and R. W. Walker, J. Chem. Soc. Faraday Trans. 1 **76**, 2374 (1980).
[9] E. W. Kaiser, J. Phys. Chem. **99**, 707 (1995).

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

$\Delta H^\circ = -149.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.5\pm2)\times10^{-29}$ [He]	295	Plumb and Ryan, 1981[1]	DF-MS (a)
7.5×10^{-29} [He]	298	Slagle, Feng, and Gutman, 1984[2]	DF-MS (b)
$1.96\times10^{-5}T^{-8.24}\exp(-2150/T)$ [He]	296–850	Wagner *et al.*, 1990[3]	PLP-MS (c)
5.9×10^{-29} [He]	298		
Relative Rate Coefficients			
$(6.5\pm2.0)\times10^{-29}$ [He]	298	Kaiser, Wallington, and Andino, 1990[4]	(d)
Reviews and Evaluations			
$1.5\times10^{-28}(T/300)^{-3.0}$ [air]	200–300	NASA, 1997[5]	(e)
$5.9\times10^{-29}(T/300)^{-3.8}$ [N_2]	200–300	IUPAC, 1997[6]	(f)

Comments

(a) Measurements at 2×10^{16}–3.4×10^{17} molecule cm^{-3} extrapolated to k_0 and k_∞ with $F_c=0.85$.

(b) Bath gas concentration 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]

(c) Experiments carried out in a heatable tubular reactor. He pressures from 0.7 to 20 mbar were used.

(d) C_2H_5 radicals were produced by UV irradiation of mixtures of Cl_2–C_2H_6–O_2. The consumed C_2H_6 was determined by either FTIR or GC with flame ionization detection (which also allowed the amount of C_2H_5Cl formed to be measured). Rate coefficients were measured as a function of pressure (4–2000 mbar) relative to that of the reaction $C_2H_5+Cl_2\rightarrow C_2H_5Cl+Cl$, and placed on an absolute basis by use of a rate coefficient of $k(C_2H_5+Cl_2)=2.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 7 mbar.

(e) Based on the measurements of Ref. 4.

(f) See Comments on Preferred Values.

Preferred Values

$k_0=5.9\times10^{-29}(T/300)^{-3.8}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

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

$\Delta n=\pm1$.

Comments on Preferred Values

We prefer the extensive results from Ref. 3 because the falloff extrapolation k_0 was done with a careful theoretical analysis. Falloff extrapolations were made with theoretically derived[3] values of $F_c=0.64$ at 200 K and 0.54 at 300 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[6]

High-pressure rate coefficients

Rate coefficient data

k_∞ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.4\pm0.5)\times10^{-12}$	295	Plumb and Ryan, 1981[1]	DF-MS (a)
4.4×10^{-12}	300	Slagle, Feng, and Gutman, 1984[2]	DF-MS (b)
$1.3\times10^{-12}\exp(420/T)$	298–400	Munk *et al.*, 1986[7]	(c)
5.3×10^{-12}	298		
$3.67\times10^{-14}T^{0.772}\exp(287/T)$	296–850	Wagner *et al.*, 1990[3]	PLP-MS (d)
7.8×10^{-12}	298		
Relative Rate Coefficients			
$(9.2\pm0.9)\times10^{-12}$	298	Kaiser, Wallington, and Andino, 1990[4]	(e)
$(8.1\pm0.3)\times10^{-12}$	260–380	Kaiser, 1995[8]	(f)
$2.9\times10^{-12}\exp(289/T)$	243–475	Dilger *et al.*, 1996[9]	(g)
7.6×10^{-12}	298		
Reviews and Evaluations			
8.0×10^{-12}	200–300	NASA, 1997[5]	(h)
7.8×10^{-12}	200–300	IUPAC, 1997[6]	(i)

Comments

(a) See comment (a) for k_0.
(b) See comment (b) for k_0.
(c) Pulse radiolysis in H_2 at 1 bar. C_2H_4 radicals were generated from the reaction of $H+C_2H_4$. $C_2H_5O_2$ radicals were monitored by absorption at 240 nm.
(d) See comment (c) for k_0.
(e) See comment (d) for k_0.
(f) Photolysis of Cl_2 in the presence of C_2H_6, O_2, and M=He or N_2 at a pressure of 760 mbar. k_∞ was measured relative to the reaction $C_2H_5+Cl_2\rightarrow C_2H_5Cl_2+Cl$ for which a rate coefficient of $1.04\times10^{-11}\times\exp(300/T)$ cm^3 molecule^{-1} s^{-1} was employed.[4,10]
(g) Muon relaxation method in longitudinal magnetic fields. $MuCH_2CH_2$ radicals were generated by addition of muonium ($Mu=\mu^+e^-$) to C_2H_4. Total pressures of N_2 varied between 1.5 and 60 bar.
(h) See comment (c) for k_0.
(i) See Comments on Preferred Values.

Preferred Values

$k=7.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_\infty=7.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

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

Comments on Preferred Values

As for k_0 we prefer the extensive data from Ref. 3 because of their combination with a careful theoretical analysis. We assume a temperature independent rate coefficient k_∞ below 300 K. Falloff curves were fitted[3] with an expression $F_c=[0.58\exp(-T/1250)+0.42\exp(-T/183)]$ which leads to $F_c=0.64$ at 200 K and 0.54 at 300 K. Within the stated error limits, the available data all agree with the preferred values based on Ref. 3. Quantum Rice–Ramsperger–Kassel (QRRK) calculations[11] of the reaction are less realistic than the RRKM calculations of Ref. 3. The analysis of the reaction system is complicated because there is a coupling of the addition reaction with the reaction forming C_2H_4, i.e., $C_2H_5+O_2\rightarrow C_2H_4+HO_2$ (see the analysis in Ref. 3). The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1997,[6] and are in good agreement with the recent measurements of Kaiser[8] and Dilger *et al.*[9]

References

[1] I. C. Plumb and K. R. Ryan, Int. J. Chem. Kinet. **13**, 1011 (1981).
[2] I. R. Slagle, Q. Feng, and D. Gutman, J. Phys. Chem. **88**, 3648 (1984).
[3] A. F. Wagner, I. R. Slagle, D. Sarzynski, and D. Gutman, J. Phys. Chem. **94**, 1853 (1990).
[4] E. W. Kaiser, T. J. Wallington, and J. M. Andino, Chem. Phys. Lett. **168**, 309 (1990).
[5] NASA Evaluation No. 12, 1997 (see references in Introduction).
[6] IUPAC, Supplement V, 1997 (see references in Introduction).
[7] J. Munk, P. Pagsberg, E. Ratajczak, and A. Sillesen, J. Phys. Chem. **90**, 2752 (1986).
[8] E. W. Kaiser, J. Phys. Chem. **99**, 707 (1995).
[9] H. Dilger, M. Schwager, P. L. W. Tregenna-Piggott, E. Roduner, I. D. Reid, D. J. Arseneau, J. J. Pan, M. Senba, M. Shelley, and D. G. Fleming, J. Phys. Chem. **100**, 6561 (1996); **100**, 16445 (1996).
[10] R. S. Timonen and D. Gutman, J. Phys. Chem. **90**, 2987 (1986).
[11] J. W. Bozzelli and A. M. Dean, J. Phys. Chem. **94**, 3313 (1990).

$n\text{-}C_3H_7 + O_2 + M \rightarrow n\text{-}C_3H_7O_2 + M$

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.5 \pm 0.9) \times 10^{-12}$	298	Ruiz and Bayes, 1984[1]	FP-MS (a)
6×10^{-12}	297	Slagle, Park, and Gutman, 1985[2]	PLP-MS (b)
Reviews and Evaluations			
8×10^{-12}	200–300	IUPAC, 1997[3]	(c)

Comments

(a) No pressure dependence detected between 1.3 and 5 mbar of He or N_2.

(b) $n\text{-}C_3H_7$ radicals were produced by CO_2 laser photolysis of $C_6F_7C_4H_9$. Only weak pressure dependences were observed over the range of He or N_2 pressures from 0.5 to 9 mbar. The rate coefficient decreased from 6×10^{-12} cm^3 molecule^{-1} s^{-1} to 2.8×10^{-13} cm^3 molecule^{-1} s^{-1} over the temperature range 297–635 K.

(c) See Comments on Preferred Values.

Preferred Values

$k = 6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1–10 mbar of air.

$k \approx k_\infty$ at 298 K and 1 bar of air.

$k_\infty = 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

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

Comments on Preferred Values

The available experimental data are consistent with each other.[1,2] Because they were obtained at total pressures below 130 mbar, we estimate that some falloff corrections have to be applied and these are taken into account in the preferred values. These values are consistent with experiments for the reactions $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ and $i\text{-}C_3H_7 + O_2 + M \rightarrow i\text{-}C_3H_7O_2 + M$ (see this evaluation). The preferred values are identical to those in our previous evaluation, IUPAC 1997.[3]

References

[1] R. P. Ruiz and K. D. Bayes, J. Phys. Chem. **88**, 2592 (1984).

[2] I. R. Slagle, J.-Y. Park, and D. Gutman, *20th International Symposium on Combustion, 1984* (Combustion Institute, Pittsburgh, 1985), pp. 733–741

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$i\text{-}C_3H_7 + O_2 + M \rightarrow i\text{-}C_3H_7O_2 + M$

$\Delta H^\circ = -158.9$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.41 \pm 0.24) \times 10^{-11}$	298	Ruiz and Bayes, 1984[1]	FP-MS (a)
8.3×10^{-12}	300	Munk *et al.*, 1986[2]	(b)
Reviews and Evaluations			
1.1×10^{-11}	200–300	IUPAC, 1997[3]	(c)

Comments

(a) No pressure dependence detected for He or N_2 pressures from 1.3 to 5 mbar.

(b) Pulse radiolysis in H_2 at 1 bar. $i\text{-}C_3H_7$ radicals were generated by the addition of H atoms to C_3H_6 and $i\text{-}C_3H_7O_2$ detected by UV absorption at 253 nm. Absorption spectrum of $i\text{-}C_3H_7$ was also detected.

(c) See Comments on Preferred Values.

Preferred Values

$k \approx k_\infty$ at 298 K and 1 bar of air.
$k_\infty = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

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

Comments on Preferred Values

The preferred values are the average of the results from Refs. 1 and 2. Falloff corrections are probably within the uncertainties of the average. The rate coefficient k_∞ for this reaction appears consistent with those for the reactions $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ and $n\text{-}C_3H_7 + O_2 + M \rightarrow n\text{-}C_3H_7O_2 + M$ (see this evaluation). The preferred values are identical to those of our previous evaluation, IUPAC, 1997.[3]

References

[1] R. P. Ruiz and K. D. Bayes, J. Phys. Chem. **88**, 2592 (1984).
[2] J. Munk, P. Pagsberg, E. Ratajczak, and A. Sillesen, Chem. Phys. Lett. **132**, 417 (1986).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$1\text{-}C_4H_9 + O_2 + M \rightarrow 1\text{-}C_4H_9O_2 + M$

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.5 \pm 1.4) \times 10^{-12}$	300	Lenhardt, McDade, and Bayes, 1980[1]	FP-MS (a)
Reviews and Evaluations			
7.5×10^{-12}	300	Atkinson, 1997[2]	(b)

Comments

(a) 1-Butyl radicals were generated by the flash photolysis of 1-butyl iodide and detected by MS. No pressure dependence of the rate coefficients was observed over the range 1.3–5.3 mbar of He.
(b) Based on the data of Lenhardt *et al.*[1]

Preferred Values

$k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is based on the study of Lenhardt *et al.*[1] Because this is the only study of this reaction, we assign large error limits. This reaction should be close to the high pressure limit at atmospheric pressure.

References

[1] T. M. Lenhardt, C. E. McDade, and K. D. Bayes, J. Chem. Phys. **72**, 304 (1980).
[2] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$2\text{-}C_4H_9 + O_2 + M \rightarrow 2\text{-}C_4H_9O_2 + M$

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.66 \pm 0.22) \times 10^{-11}$	300	Lenhardt, McDade, and Bayes, 1980[1]	FP-MS (a)
Reviews and Evaluations			
1.66×10^{-11}	300	Atkinson, 1997[2]	(b)

Comments

(a) 2-Butyl radicals were generated by the flash photolysis of 2-butyl iodide and detected by MS. No pressure dependence of the rate coefficients was observed over the range 1.3–5.3 mbar of He.

(b) Based on the data of Lenhardt *et al.*[1]

Preferred Values

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

Reliability

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

Comments on Preferred Values

The preferred value is based on the study of Lenhard *et al.*[1]

References

[1] T. M. Lenhardt, C. E. McDade, and K. D. Bayes, J. Chem. Phys. **72**, 304 (1980).

[2] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$CH_3COCH_2 + O_2 + M \rightarrow CH_3COCH_2O_2 + M$

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.45×10^{-12}	298	Cox *et al.*, 1990[1]	(a)
Reviews and Evaluations			
1.5×10^{-12}	298	IUPAC, 1997[2]	(b)

Comments

(a) Pulse radiolysis of CH_3COCH_2–O_2–SF_6 mixtures at 1 bar of SF_6. CH_3COCH_2 radicals were formed from the reaction of F atoms with CH_3COCH_3. At the monitoring wavelength of 310 nm both CH_3COCH_2 and $CH_3COCH_2O_2$ absorb, with the absorption cross section of the peroxy radical being a factor of 1.7 greater than that of the CH_3COCH_2 radical. The rate coefficient was evaluated by simulations of the above reaction together with the reaction $CH_3COCH_2 + CH_3COCH_2O_2 \rightarrow 2CH_3COCH_2O$.

(b) See Comments on Preferred Values.

Preferred Values

$k \approx k_\infty$ at 298 K and 1 bar of air.

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

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 300 K.

Comments on Preferred Values

The preferred values are based on the study of Cox *et al.*[1] Because this is the only study of this reaction, we assign large error limits. Near atmospheric pressure this reaction should be close to the high pressure limit. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[2]

References

[1] R. A. Cox, J. Munk, O. J. Nielsen, P. Pagsberg, and E. Ratajczak, Chem. Phys. Lett. **173**, 206 (1990).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$HCO + O_2 \rightarrow CO + HO_2$

$\Delta H^\circ = -139.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.6\pm0.9)\times10^{-12}$	300	Shibuya *et al.*, 1977[1]	FP-AS (a)
$5.5\times10^{-11}\ T^{-(0.4\pm0.3)}$	298–503	Veyret and Lesclaux, 1981[2]	FP-AS (b)
$(5.6\pm0.6)\times10^{-12}$	298		
$(4.65\pm0.6)\times10^{-12}$	295	Langford and Moore, 1984[3]	PLP-AS (c)
$1.3\times10^{-11}\exp[-(204\pm180)/T]$	295–713	Timonen, Ratajczak, and Gutman, 1988[4]	PLP-MS (d)
6.2×10^{-12}	295		
$3.2\times10^{-12}\exp(87/T)$	200–398	Stief, Nesbitt, and Gleason, 1990[5]	DF-MS (e)
4.3×10^{-12}	298		
$4.3\times10-12$	298	Dóbé, Wagner, and Ziemer, 1995[6]	DF-LMR (f)
Relative Rate Coefficients			
$(5.7\pm1.2)\times10^{-12}$	297	Washida, Martinez, and Bayes, 1974[7]	RR (g)
Reviews and Evaluations			
5.0×10^{-12}	300–2500	Baulch *et al.*, 1992[8]	(h)
$3.5\times10^{-12}\exp(140/T)$	298–503	NASA, 1997[9]	(i)
5.5×10^{-12}	200–400	IUPAC, 1997[10]	(j)

Comments

(a) Flash photolysis of CH_3CHO–O_2 mixtures; HCO monitored by time-resolved absorption at 613.8 nm. There was no pressure effect on k for pressures of up to 690 mbar (520 Torr) of He.

(b) Flash photolysis of HCHO and CH_3CHO; HCO was monitored by laser absorption at 614.5 nm at total pressures of 17–660 mbar (13–500 Torr).

(c) Pulsed laser photolysis of HCHO or $(CHO)_2$ with monitoring of HCO by absorption at total pressures of up to 1330 mbar (1000 Torr).

(d) Pulsed laser photolysis of CH_3CHO; HCO was monitored by photoionization MS at pressures of 0.69–1.22 mbar (0.52–0.92 Torr).

(e) Discharge-flow system. HCO radicals were generated from Cl+HCHO and monitored by photoionization MS.

(f) HCO radicals were generated by the reaction of F atoms with HCHO. The total pressure was 1.7 mbar of He. The yield of HO_2 radicals was measured relative to the formation yield of HO_2 radicals from the reaction of F atoms with H_2O_2, and determined to be 1.00 ±0.05.

(g) Discharge flow system with HCO being monitored by photoionization MS. k measured relative to $k(O+HCO\rightarrow\text{products}) = 2.1\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (measured in the same apparatus) by observing the effect of O_2 on [HCO] in a flowing mixture of O_2–C_2H_4; $k/k(O+HCO) = (2.74\pm0.21)\times10^{-2}$.

(h) Based on the data of Veyret and Lesclaux[2] and Timonen *et al.*[4]

(i) Based on the data of Shibuya *et al.*,[1] Veyret and Lesclaux,[2] Langford and Moore,[3] and Washida *et al.*[7]

(j) Based on the data of Shibuya *et al.*,[1] Veyret and Lesclaux,[2] Timonen *et al.*,[4] Stief *et al.*,[5] and Washida *et al.*[7]

Preferred Values

$k = 5.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k = \pm0.15$ at 298 K.
$\Delta(E/R) = \pm150$ K.

Comments on Preferred Values

The preferred temperature-independent rate coefficient is the average of the room-temperature rate coefficients of Shibuya *et al.*,[1] Veyret and Lesclaux,[2] Langford and Moore,[3] Timonen *et al.*,[4] Stief *et al.*,[5] Dóbé *et al.*,[6] and Washida *et al.*[7] Taken together, the temperature-dependent studies of Veyret and Lesclaux,[2] Timonen *et al.*,[4] and Stief *et al.*[5] show that the rate coefficient of this reaction is essentially independent of temperature over the range 200–400 K, within the error limits of the measurements.

References

[1] K. Shibuya, T. Ebata, K. Obi, and I. Tanaka, J. Phys. Chem. **81**, 2292 (1977).

[2] B. Veyret and R. Lesclaux, J. Phys. Chem. **85**, 1918 (1981).

[3] A. O. Langford and C. B. Moore, J. Chem. Phys. **80**, 4211 (1984).

[4] R. S. Timonen, E. Ratajczak, and D. Gutman, J. Phys. Chem. **92**, 651 (1988).
[5] L. J. Stief, F. L. Nesbitt, and J. F. Gleason, Abstracts of papers presented at the International Symposium of Gas Kinetics, Assisi, Italy, September 1990.
[6] S. Dóbé, H. G. Wagner, and H. Ziemer, React. Kinet. Catal. Lett. **54**, 271 (1995).
[7] N. Washida, R. I. Martinez, and K. D. Bayes, Z. Naturforsch **29a**, 251 (1974).
[8] D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Franck, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, J. Phys. Chem. Ref. Data **21**, 411 (1992).
[9] NASA Evaluation No. 12, 1997 (see references in Introduction).
[10] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3CO + O_2 + M \rightarrow CH_3C(O)O_2 + M$

$\Delta H° = -162\ kJ \cdot mol^{-1}$

High-pressure rate coefficients

Rate coefficient data

$k_\infty/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.0\pm0.4)\times10^{-12}$	298	McDade, Lenhardt, and Bayes, 1982[1]	(a)
$(3.0\pm0.6)\times10^{-12}$	296	Kaiser and Wallington, 1995[4]	RR (b)
$(3.2\pm0.6)\times10^{-12}$	298	Tyndall *et al.*, 1997[3]	RR (c)
$(3.3\pm0.6)\times10^{-12}$	228		
Reviews and Evaluations			
2.0×10^{-12} (1.3–5 mbar)	298	IUPAC, 1997[4]	(d)
5.0×10^{-12}	200–300		

Comments

(a) Flow system with CH_3CO generated from pulsed photolysis of CH_3COCH_3 or $CH_3COCH_2COCH_3$. $[CH_3CO]$ was monitored by photoionization mass spectrometry and kinetics evaluated from pseudofirst-order decays of CH_3CO. The pressure range was 1.3–5 mbar.

(b) Measurement of the rate coefficient ratio for $k(CH_3CO+Cl_2)/k(CH_3CO+O_2)=7.9\pm0.5$ at 930 mbar total pressure. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(CH_3CO+Cl_2)=2.4\times10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$.[5]

(c) Measurement of the rate coefficient ratios $k(CH_3CO+Cl_2)/k(CH_3CO+O_2)$ at 228 and 298 K over the pressure range 0.13–1460 mbar. The rate constant k was observed to increase with increasing pressure, with the rate coefficient k approaching the high-pressure limit above ~400 mbar. The rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(CH_3CO+Cl_2)=2.8\times10^{-11} \times\exp(-47/T)\ cm^3\ molecule^{-1}\ s^{-1}$.[5]

(d) Based on Ref. 1, with some falloff correction estimated by comparison to the reaction $C_2H_5+O_2+M \rightarrow C_2H_5O_2+M$ (this evaluation).

Preferred Values

$k_\infty=3.2\times10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$, independent of temperature over the range 220–300 K.

Reliability

$\Delta \log k_\infty=\pm0.2$ over the temperature range 220–300 K.

Comments on Preferred Values

The preferred values are based on the data of Kaiser and Wallington[2] and Tyndall *et al.*[3]

References

[1] C. E. McDade, T. M. Lenhardt, and K. D. Bayes, J. Photochem. **20**, 1 (1982).
[2] E. W. Kaiser and T. J. Wallington, J. Phys. Chem. **99**, 8669 (1995).
[3] G. S. Tyndall, J. J. Orlando, T. J. Wallington, and M. D. Hurley, Int. J. Chem. Kinet. **29**, 655 (1997).
[4] IUPAC, Supplement IV, 1997 (see references in Introduction).
[5] M. M. Maricq and J. J. Szente, Chem. Phys. Lett. **253**, 333 (1996).

$CH_2OH + O_2 \rightarrow HCHO + HO_2$

$\Delta H° = -76.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.5 \pm 2.5) \times 10^{-12}$	298	Grotheer *et al.*, 1985[1]	DF-MS (a)
$(10.6 \pm 2.5) \times 10^{-12}$	296	Dobé *et al.*, 1985[2]	DF-LMR (b)
$(10.5 \pm 4.7) \times 10^{-12}$	296		
$(8.6 \pm 2.0) \times 10^{-12}$	298	Payne *et al.*, 1988[3]	DF-MS (c)
$\{2.5 \times 10^{-9}\ T^{-1.0} + 4.0 \times 10^{-10} \exp(-2525/T)\}$	370–684	Grotheer *et al.*, 1988[4]	DF-MS (d)
$5.6 \times 10^{-9} \exp(-1700/T)$	215–250	Nesbitt, Payne, and Stief, 1988[5]	DF-MS (e)
$(8.61 \pm 1.14) \times 10^{-12}$	300		
$(8.8 \pm 0.2) \times 10^{-12}$	298	Pagsberg *et al.*, 1989[6]	PR-AS (f)
$(1.17 \pm 0.12) \times 10^{-11}$	296	Miyoshi *et al.*, 1990[7]	PLP-MS (g)
Reviews and Evaluations			
9.1×10^{-12}	250–300	NASA, 1997[8]	(h)
9.4×10^{-12}	298	IUPAC, 1997[9]	(i)

Comments

(a) CH_2OH was generated from $Cl+CH_3OH$ at total pressures of 0.4–1.2 mbar (0.3–0.9 Torr). k was derived from the rate of disappearance of CH_2OH in excess O_2 by MS.

(b) CH_2OH was generated from $F+CH_3OH$ at total pressures of 0.69–6.5 mbar (0.52–4.9 Torr). Two values of k were derived from the rate of disappearance of CH_2OH and of the appearance of HO_2, both monitored by LMR spectroscopy.

(c) CH_2OH was generated from $Cl+CH_3OH$ at total pressures of ~1.3 mbar (~1 Torr). k was derived from the rate of disappearance of CH_2OH in excess O_2 by MS.

(d) As for comment (a) at pressures of ~1.1 mbar (~0.8 Torr).

(e) As for comment (c) at pressures of ~1.3 mbar (~1 Torr).

(f) CH_2OH was generated from $F+CH_3OH$ at total pressures of 1 bar (760 Torr). k was derived from the rate of disappearance of CH_2OH in excess of O_2 by absorption at 285.5 nm.

(g) Pulsed laser photolysis of CH_3COCH_2OH, with the decay of CH_2OH being monitored by photoionization MS, at total pressures of 1.7–7.3 mbar (1.3–5.5 Torr).

(h) Based on the data of Grotheer *et al.*,[1] Dóbé *et al.*,[2] Payne *et al.*,[3] Grotheer *et al.*,[4] and Nesbitt *et al.*[5]

(i) See Comments on Preferred Values, but with k_{298} including the extrapolated data of Grotheer *et al.*[4]

Preferred Values

$k = 9.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.

Comments on Preferred Values

The rate coefficient at 298 K is now well established for this reaction, and our recommendation is the average of the results of Grotheer *et al.*,[1] Dóbé *et al.*,[2] Payne *et al.*,[3] Nesbitt *et al.*,[5] Pagsberg *et al.*,[6] and Miyoshi *et al.*[7] The earlier data of Wang *et al.*[10] and Radford *et al.*[11] are rejected on the basis that they involved high concentrations of radicals, leading to mechanistic complications.[11] The two studies[4,5] of the temperature dependence of this reaction indicate that the rate coefficient follows a complicated non-Arrhenius behavior over the range 200–700 K. The existing data are difficult to explain and more work is needed to confirm the observed temperature dependence of this reaction before a recommendation can be made.

Grotheer *et al.*[4] have carried out experiments replacing CH_3OH by CH_3OD and have observed no kinetic isotope effect for the CH_2OH/CH_2OD+O_2 reactions.

References

[1] H.-H. Grotheer, G. Riekert, U. Meier, and Th. Just, Ber. Bunsenges. Phys. Chem. **89**, 187 (1985).

[2] S. Dóbé, F. Temps, T. Böhland, and H. Gg. Wagner, Z. Naturforsch. **40A**, 1289 (1985).

[3] W. A. Payne, J. Brunning, M. B. Mitchell, and L. J. Stief, Int. J. Chem. Kinet. **20**, 63 (1988).

[4] H.-H. Grotheer, G. Riekert, D. Walter, and Th. Just, J. Phys. Chem. **92**, 4028 (1988); *22nd International Symposium on Combustion, 1988* (Combustion Institute, Pittsburgh, PA, 1989), pp. 963–972.

[5] F. L. Nesbitt, W. A. Payne, and L. J. Stief, J. Phys. Chem. **92**, 4030 (1988).

[6] P. Pagsberg, J. Munk, C. Anastasi, and V. J. Simpson, J. Phys. Chem. **93**, 5162 (1989).

[7] A. Miyoshi, H. Matsui, and N. Washida, J. Phys. Chem. **94**, 3016 (1990).

[8] NASA Evaluation No. 12, 1997 (see references in Introduction).

[9] IUPAC, Supplement V, 1997 (see references in Introduction).

[10] W. C. Wang, M. Suto, and L. C. Lee, J. Chem. Phys. **81**, 3122 (1984).

[11] H. E. Radford, Chem. Phys. Lett. **71**, 195 (1980).

$CH_3CHOH + O_2 \rightarrow CH_3CHO + HO_2$

$\Delta H° = -87.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comment
Absolute Rate Coefficients			
$\{1.4\times10^{-8}\ T^{-1.2}$ $+8.0\times10^{-10}\exp(-2525/T)\}$	300–682	Grotheer *et al.*, 1988[1]	DF-MS (a)
1.56×10^{-11}	300		
$(1.3\pm0.2)\times10^{-11}$	300	Anastasi *et al.*, 1989[2]	PR-AS (b)
$(2.8\pm0.2)\times10^{-11}$	293	Miyoshi, Matsui, and Washida, 1989[3]	PLP-MS (c)
Reviews and Evaluations			
1.9×10^{-11}	298	IUPAC, 1997[4]	(d)

Comments

(a) CH_3CHOH was generated from $Cl+C_2H_5OH$ in the presence of a large excess of O_2 at total pressures of ~1 mbar (~0.8 Torr). The rate coefficient k was derived from the disappearance of CH_3CHOH, as monitored by low electron energy MS.

(b) Pulse radiolysis of Ar–SF_6–HCl–C_2H_5OH–O_2 mixtures at total pressures of 1 bar (760 Torr) and with $[SF_6]\gg[HCl]\gg[C_2H_5OH]\gg[O_2]$. CH_3CHOH was generated from $Cl+C_2H_5OH$ and monitored by UV absorption at 260 nm.

(c) Pulsed laser photolysis of $CH_3COCHOHCH_3$ in a large excess of He at total pressures of 2.7–9.3 mbar (2–7 Torr). CH_3CHOH was monitored by photoionization MS in the presence of excess O_2.

(d) See Comments on Preferred Values.

Preferred Values

$k = 1.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value of k_{298} is the mean of the results o Grotheer *et al.*,[1] Anastasi *et al.*,[2] and Miyoshi *et al.*,[3] and i unchanged from our previous evaluation.[4] The rather larg discrepancy between the data of Miyoshi *et al.*[3] and the othe two studies[1,2] could be due to the different sources of generation of the CH_3CHOH radical. CH_3CHOH radica generation[1,2] involving Cl attack on C_2H_5OH may not be a clean a source as is the photolysis[3] of $CH_3COCHOHCH_3$.

The temperature dependence of the rate coefficient determined by Grotheer *et al.*[1] shows a marked non-Arrheniu behavior, but this needs to be confirmed before a recommendation can be made. Evidence for the reaction betwee CH_3CHOH and O_2 yielding CH_3CHO as a major produc comes from the product study of the photooxidation of ethanol by Carter *et al.*[5]

References

[1] H.-H. Grotheer, G. Riekert, D. Walter, and Th. Just, *22nd Internationa Symposium on Combustion, 1988* (Combustion Institute, Pittsburgh, PA 1989), pp. 963–972.

[2] C. Anastasi, V. Simpson, J. Munk, and P. Pagsberg, Chem. Phys. Lett **164**, 18 (1989).

[3] A. Miyoshi, H. Matsui, and N. Washida, Chem. Phys. Lett. **160**, 29 (1989).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

[5] W. P. L. Carter, K. R. Darnall, R. A. Graham, A. M. Winer, and J. N Pitts, Jr., J. Phys. Chem. **83**, 2305 (1979).

$CH_2CH_2OH + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comment
Absolute Rate Coefficients			
$(3.0\pm0.4)\times10^{-12}$	293	Miyoshi, Matsui, and Washida, 1989	PLP-MS (a)
Reviews and Evaluations			
3.0×10^{-12}	298	IUPAC, 1997[2]	(b)

Comments

(a) Pulsed laser photolysis of $ClCH_2CH_2OH$ and $BrCH_2CH_2OH$ in a large excess of He at total pressures of 2.7–9.3 mbar (2–7 Torr). CH_2CH_2OH radicals were monitored by photoionization MS in the presence of excess O_2.

(b) See Comments on Preferred Values.

Preferred Values

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

Reliability

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

Comments on Preferred Values

The direct measurements[1] of this rate coefficient, from the pulsed laser photolysis of either $ClCH_2CH_2OH$ or $BrCH_2CH_2OH$ as the radical source, showed a good level of consistency. By analogy with the reactions $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ and $CH_3CO + O_2 + M \rightarrow CH_3CO_3 + M$ (this evaluation), the rate coefficient for this reaction is expected to be close to the high-pressure limit under the experimental conditions employed. The UV absorption spectrum of the $HOCH_2CH_2O_2$ radical has been observed[3,4] by pulse radiolysis of SF_6–H_2O mixtures[3] and pulsed laser photolysis of H_2O_2 in the presence of C_2H_4 and O_2.[4] These observations indicate that the reaction between CH_2CH_2OH radicals and O_2 leads predominantly to the adduct peroxy radical. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[2]

References

[1] A. Miyoshi, H. Matsui, and N. Washida, Chem. Phys. Lett. **160**, 291 (1989).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

[3] C. Anastasi, D. J. Muir, V. J. Simpson, and P. Pagsberg, J. Phys. Chem. **95**, 5791 (1991).

[4] T. P. Murrells, M. E. Jenkin, S. J. Shalliker, and G. D. Hayman, J. Chem. Soc. Faraday Trans. **87**, 2351 (1991).

$CH_3O + O_2 \rightarrow HCHO + HO_2$

$\Delta H° = -111.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.05 \times 10^{-13} \exp(-1310/T)$	413–608	Gutman, Sanders, and Butler, 1982[1]	PLP-LIF (a)
1.3×10^{-15}	298*		
$5.5 \times 10^{-14} \exp(-1000/T)$	298–450	Lorenz *et al.*, 1985[2]	PLP-LIF (b)
1.9×10^{-15}	298		
$2.3 \times 10^{-14}(1000/T)^{-9.5} \exp(2768/T)$	298–973	Wantuck *et al.*, 1987[3]	PLP-LIF (c)
2.1×10^{-15}	298		
Reviews and Evaluations			
$6.7 \times 10^{-14} \exp(-1070/T)$	300–1000	Baulch *et al.*, 1992[4]	(d)
$3.9 \times 10^{-14} \exp(-900/T)$	298–608	NASA, 1997[5]	(e)
$7.2 \times 10^{-14} \exp(-1080/T)$	290–610	IUPAC, 1997[6]	(f)

Comments

(a) CH_3O generated from pulsed laser photolysis of CH_3ONO at 266 nm. $[CH_3O]$ was monitored by LIF at a total pressure of 53 mbar (40 Torr).

(b) Pulsed laser photolysis of CH_3ONO with monitoring of CH_3O by LIF, at pressures of 100 mbar (75 Torr) of He. At 298 K the rate coefficient was shown to be independent of pressure over the range 10–200 mbar (7.5–150 Torr) of He.

(c) Pulsed laser photolysis of CH_3OH or CH_3ONO at 193 nm in the presence of O_2 plus 33 mbar (25 Torr) of Ar. CH_3O radicals were monitored by LIF. Non-Arrhenius behavior was observed over entire temperature range and fitted by the cited empirical equation. Rate coefficients combined with the data of Gutman *et al.*[1] and Lorenz *et al.*[2] were found to obey a double exponential expression, with $k = \{1.5 \times 10^{-10} \exp(-6028/T) + 3.6 \times 10^{-14} \exp(-880/T)\}$ cm^3 molecule^{-1} s^{-1}.

(d) Obtained by a least-squares fit to the data of Gutman *et al.*[1] and Lorenz *et al.*[2]

(e) Based on the data of Gutman *et al.*[1] and Lorenz *et al.*[2]

(f) See Comments on Preferred Values.

Preferred Values

$k = 1.9 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.2 \times 10^{-14} \exp(-1080/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–610 K.

Reliability

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

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

Comments on Preferred Values

The direct measurements of the rate coefficients by Lorenz *et al.*[2] (298–450 K) and Wantuck *et al.*[3] (298–973 K) are in good agreement with the similar measurements of Gutman *et al.*[1] (413–608 K), where the temperature ranges overlap. The preferred values are derived from a least-mean-squares analysis of these three sets of data[1–3] over the temperature range 298–608 K, and are unchanged from our previous evaluation.[6] The higher temperature measurements of Wantuck *et al.*[3] give a clear indication of non-Arrhenius behavior over the extended temperature range. The anomalously low *A* factor for a simple H-atom transfer reaction and the possibility of a more complicated mechanism have both been noted.[5]

References

[1] D. Gutman, N. Sanders, and J. E. Butler, J. Phys. Chem. **86**, 66 (1982).

[2] K. Lorenz, D. Rhäsa, R. Zellner, and B. Fritz, Ber. Bunsenges. Phys. Chem. **89**, 341 (1985).

[3] P. J. Wantuck, R. C. Oldenborg, S. L. Baughcum, and K. R. Winn, J. Phys. Chem. **91**, 4653 (1987).

[4] D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Franck, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, J. Phys. Chem. Ref. Data **21**, 411 (1992).

[5] NASA Evaluation No. 12, 1997 (see references in Introduction).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$

$\Delta H° = 135.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
8.0×10^{-15}	296	Gutman, Sanders, and Butler, 1982[1]	PLP-LIF (a)
9.8×10^{-15}	353		
$7.1\times10^{-14}\exp[(-552\pm64)/T]$	295–411	Hartmann *et al.*, 1990[2]	PLP-LIF (b)
$(1.08\pm0.20)\times10^{-14}$	295		
Reviews and Evaluations			
$1.0\times10^{-13}\exp(-830/T)$	300–1000	Baulch *et al.*, 1992[3]	(c)
$6.3\times10^{-14}\exp(-550/T)$	295–411	NASA, 1997[4]	(d)
$6.0\times10^{-14}\exp(-550/T)$	295–425	IUPAC, 1997[5]	(e)

Comments

(a) Pulsed laser photolysis of C_2H_5ONO at 266 nm, with C_2H_5O radicals being monitored by LIF at a total pressure of 53 mbar (40 Torr).

(b) Pulsed laser photolysis of C_2H_5ONO at 266 nm in $C_2H_5ONO-O_2-He$ mixtures, with LIF monitoring of C_2H_5O radicals in the wavelength range 310–330 nm. Studies were carried out at a total pressure of 35 mbar (26 Torr).

(c) Based on the mean values of k_{298} of Gutman *et al.*[1] and Zabarnick and Heicklen,[6] assuming that the *A* factor is the same as that of the reaction $CH_3O + O_2 \rightarrow HCHO + HO_2$.

(d) Based on the studies of Gutman *et al.*[1] and Hartmann *et al.*[2]

(e) See Comments on Preferred Values.

Preferred Values

$k = 9.5\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.0\times10^{-14}\exp(-550/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–420 K.

Reliability

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

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

Comments on Preferred Values

The preferred 298 K rate coefficient and the temperature dependence are obtained from the mean of the room-temperature rate coefficients of Gutman *et al.*[1] (296 K) and of Hartmann *et al.*[2] (295 K) and by taking the rounded-off value of *E/R* of Hartmann *et al.*[2] The rate coefficients of Gutman *et al.*[1] and of Hartmann *et al.*[2] differ by 30%–50% which, although within the range of the individual error limits, is somewhat higher than might be expected from two direct studies. The relative rate measurements of Zabarnick and Heicklen[6] yield a value of k_{298} which is consistent with the preferred value within the recommended error limits.

It should be noted that the *A* factor for the above reaction is very low, but in keeping with that for the analogous reaction $CH_3O+O_2 \rightarrow HCHO+HO_2$. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

References

[1] D. Gutman, N. Sanders, and J. E. Butler, J. Phys. Chem. **86**, 66 (1982).

[2] D. Hartmann, J. Karthäuser, J. P. Sawerysyn, and R. Zellner, Ber. Bunsenges. Phys. Chem. **94**, 639 (1990).

[3] D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Franck, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, J. Phys. Chem. Ref. Data **21**, 411 (1992).

[4] NASA Evaluation No. 12, 1997 (see references in Introduction).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

[6] S. Zabarnick and J. Heicklen, Int. J. Chem. Kinet. **17**, 455 (1985).

$1\text{-}C_3H_7O + O_2 \rightarrow C_2H_5CHO + HO_2$

$\Delta H° = -131.4\ kJ \cdot mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.4\times10^{-14}\ \exp[-(108\pm61)/T]$	223–303	Mund, Fockenberg, and Zellner, 1998[1]	PLP-LIF (a)
9.8×10^{-15}	298		
Relative Rate Coefficients			
$2.8\times10^{-13}\ \exp[-(879\pm117)/T]$	247–393	Zabarnick and Heicklen, 1985[2]	RR (b)
1.5×10^{-14}	298		
Reviews and Evaluations			
8×10^{-15}	298	IUPAC, 1997[3]	(c)

Comments

(a) The temperature range covered and the 298 K rate coefficient were obtained from graphical presentation.[1]

(b) Photolysis at 366 nm of $n\text{-}C_3H_7ONO$ in a static system in the presence of NO, O_2, and N_2 at total pressures of >200 mbar (>150 Torr). Rate data were based on the measured quantum yields of C_2H_5CHO product. The rate coefficient k was measured relative to $n\text{-}C_3H_7O+NO \rightarrow$ products with $k(n\text{-}C_3H_7O+O_2)/k(n\text{-}C_3H_7O+NO) = 6.8\times10^{-3}\exp(-879/T)$, and is placed on an absolute basis by use of $k(n\text{-}C_3H_7O+NO) = 4.1\times10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$, independent of temperature. This latter value is based on the measured data for the reactions $i\text{-}C_3H_7O+NO+M \rightarrow i\text{-}C_3H_7ONO+M$ and $i\text{-}C_3H_7O+NO \rightarrow (CH_3)_2CO+HNO$ (this evaluation).

(c) Based on measured rate coefficients for the analogous reactions of C_2H_5O and $2\text{-}C_3H_7O$ radicals with O_2.

Preferred Values

$k = 9.7\times10^{-15}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k = 1.4\times10^{-14}\exp(-110/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 220–310 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are based on the sole absolute rate study of Mund *et al.*[1] The 298 K preferred rate coefficient is essentially identical to that of the analogous reaction of the C_2H_5O radical with O_2 (see data sheet, this evaluation). The rate coefficients derived from the relative rate study of Zabarnick and Heicklen[2] are in significant disagreement with the absolute rate data.[1]

References

[1] Ch. Mund, Ch. Fockenberg, and R. Zellner, Ber. Bunsenges. Phys. Chem. **102**, 709 (1998).

[2] S. Zabarnick and J. Heicklen, Int. J. Chem. Kinet. **17**, 477 (1985).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$2\text{-}C_3H_7O + O_2 \rightarrow CH_3COCH_3 + HO_2$

$\Delta H° = -150.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.51\times10^{-14}\exp[-(200\pm140/T)]$	294–384	Balla, Nelson, and McDonald, 1985[1]	PLP-LIF (a)
7.72×10^{-15}	298		
$1.0\times10^{-14}\exp[-(217\pm49)/T]$	218–313	Mund, Fockenberg, and Zellner, 1998[2]	PLP-LIF (b)
6.5×10^{-15}	298		
Reviews and Evaluations			
$1.5\times10^{-14}\exp(-200/T)$	290–390	IUPAC, 1997[3]	(c)

Comments

(a) Pulsed laser photolysis of 2-propyl nitrite at 355 nm, with LIF detection of $2\text{-}C_3H_7O$ radicals. The pressure range was 1.3–67 mbar (1–50 Torr).

(b) The 298 K rate coefficient was obtained from the graphical presentation.[2]

(c) Based on the study of Balla *et al.*[1]

Preferred Values

$k = 7.2\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.4\times10^{-14}\exp(-210/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210–390 K.

Reliability

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

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

Comments on Preferred Values

The results of Balla *et al.*[1] and Mund *et al.*[2] are in good agreement. The preferred values are based on an average of the 298 K rate coefficients and the values of E/R, with the pre-exponential factor being calculated to fit the room temperature rate coefficient.

References

[1] R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **99**, 32 (1985).
[2] Ch. Mund, Ch. Fockenberg, and R. Zellner, Ber. Bunsenges. Phys. Chem **102**, 709 (1998).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3CH_2CH_2CH_2O + O_2 \rightarrow CH_3CH_2CH_2CHO + HO_2$

$\Delta H° = -127.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
7.7×10^{-15}	298	Hoffmann, Mörs, and Zellner, 1992;[1] Zellner, 1994[2]	PLP-LIF (a)
Relative Rate Coefficients			
$6.8\times10^{-13}\exp[-(1178\pm176)/T]$	265–393	Morabito and Heicklen, 1987[3]	RR (b)
1.3×10^{-14}	298		
Reviews and Evaluations			
9.5×10^{-15}	298	Atkinson, 1997[4]	(c)

Comments

(a) Pulsed laser photolysis of Cl_2 in the presence of $n\text{-}C_4H_{10}\text{–}O_2\text{–}NO$ mixtures in a flow system at total pressures of 13–67 mbar (10–50 Torr). Time-resolved monitoring of OH radicals was carried out by cw–laser absorption, and of NO_2 by LIF. The rate coefficient was derived from a computer simulation of OH radical and NO_2 temporal profiles.

(b) Photolysis of 1-butyl nitrite at 366 nm in the presence of NO and O_2. Rate data were derived from the quantum yields of product formation, and a rate coefficient ratio of $k(1\text{-}C_4H_9O+O_2)/k(1\text{-}C_4H_9O+NO)=1.67\times10^{-2}\exp[-(1178\pm176)/T]$ was obtained. This rate coefficient ratio is placed on an absolute basis using a rate coefficient of $k(1\text{-}C_4H_9O+NO)=4.1\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, independent of temperature (see data sheet for $2\text{-}C_3H_7O+NO$, this evaluation).

(c) Estimate based on data for C_2H_5O reaction with O_2 assuming that $k(RCH_2O+O_2)=6.0\times10^{-14}\times\exp(-550/T)$ cm^3 $molecule^{-1}$ s^{-1} for all RCH_2O radicals.

Preferred Values

$k=9.5\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$k=6.0\times10^{-14}\exp(-550/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 290–400 K.

Reliability

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

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

Comments on Preferred Values

We have accepted the recommendation of Atkinson[4] for the preferred values, which was an estimate based on absolute rate data for the analogous reaction of the C_2H_5O radical. While this recommendation is supported by the indirect studies of Zellner,[2] it is desirable that direct measurements of the rate coefficients of this reaction are carried out. As for the $1\text{-}C_3H_7O+O_2$ reaction, the relative rate data of Morabito and Heicklen[3] are in significant disagreement with the absolute rate data.[1,2]

References

[1] A. Hoffmann, V. Mörs, and R. Zellner, Ber. Bunsenges. Phys. Chem. **96**, 437 (1992).

[2] R. Zellner, data cited in Table 12, p. 60, of EUROTRAC Annual Report 1993, Part 8, LACTOZ, International Scientific Secretariat Fraunhofer Institute (IFU), Garmisch-Partenkirchen, Germany, July, 1994.

[3] P. Morabito and J. Heicklen, Bull. Chem. Soc. Jpn. **60**, 2641 (1987).

[4] R. Atkinson, Int. J. Chem. Kinet. **29**, 99 (1997).

$CH_3CH_2CH_2CH_2O + M \rightarrow CH_2CH_2CH_2CH_2OH + M$

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
1.6×10^5	303	Carter *et al.*, 1979[1]	S-GC (a)
$(1.4\pm0.5)\times10^5$	296	Cox, Patrick, and Chant, 1981[2]	S-GC (b)
$(1.8\pm0.2)\times10^5$	298	Niki *et al.*, 1981[3]	S-FTIR (c)
Reviews and Evaluations			
$2.4\times10^{11}\exp(-4170/T)$		Atkinson, 1997[4]	(d)

Comments

(a) Smog chamber photolyses of $n\text{-}C_4H_{10}\text{–}NO_x$–air mixtures at 1 bar pressure. End-product analyses of C_3H_7CHO by GC. $k/k(1\text{-}C_4H_9O+O_2)=1.6\times10^{19}$ molecule cm^{-3} obtained from yields of C_3H_7CHO and the rate of disappearance of $n\text{-}C_4H_{10}$. The above value of k is calculated by using a rate coefficient of $k=9.5\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} for the reference reaction $1\text{-}C_4H_9O+O_2\rightarrow C_3H_7CHO+HO_2$ at 298 K (this evaluation).

(b) Smog chamber photolysis of $n\text{-}C_4H_{10}$–HONO–air mixtures at 1 bar (760 Torr) pressure. End-product analysis of C_3H_7CHO by GC. $k/k(1\text{-}C_4H_9O+O_2)=(1.5\pm0.5)\times10^{19}$ molecule cm^{-3} was derived from the yields of C_3H_7CHO and the rate of disappearance of $n\text{-}C_4H_{10}$ as a function of $[O_2]$. Above value of k was calculated by using a rate coefficient of $k=9.5\times10^{-15}$ cm^{-3} $molecule^{-1}$ s^{-1} for the reference reaction, $1\text{-}C_4H_9O+O_2\rightarrow C_3H_7CHO+HO_2$ at 298 K (this evaluation).

(c) Photolysis of $1\text{-}C_4H_9ONO$–air mixtures at 930 mbar (700 Torr) pressure in an FTIR cell. $k/k(1\text{-}C_4H_9O+O_2)=(1.9\pm0.2)\times10^{19}$ molecule cm^{-3} was derived from yields of C_3H_7CHO and the rate of disappearance of $1\text{-}C_4H_9ONO$. Above value of k calculated using a rate coefficient of $k=9.5\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} for the reference reaction, $1\text{-}C_4H_9O+O_2\rightarrow C_3H_7CHO+HO_2$, at 298 K (this evaluation).

(d) Derived from the rounded-off mean experimental value[1–3] of $k\sim2\times10^5$ s^{-1} at 298 K and a transition-state-theory estimate[5] of $A\cong2.4\times10^{11}$ s^{-1}.

Preferred Values

$k=1.6\times10^5$ s^{-1} at 298 K and 1 bar pressure.

$k=2.4\times10^{11}\exp(-4240/T)$ s^{-1} over the temperature range 295–400 K and 1 bar pressure.

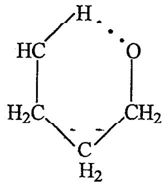
Reliability

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

$\Delta(E/R)=\pm1000$ K.

Comments on Preferred Values

The preferred rate coefficient at room temperature is the mean from the studies of Carter *et al.*,[1] Cox *et al.*,[2] and Niki *et al.*[3] The preferred *A* factor is an estimate of Baldwin *et al.*[5] from transition-state theory on the basis of a mechanism involving a 1,5-H-atom shift:



The preferred value of $E/R=4240$ K follows from the preferred values of k_{298} and the *A* factor. Large uncertainties have been assigned to these preferred values and direct measurements of the rate coefficient and its temperature coefficient are needed.

This procedure for obtaining the preferred rate parameters follows the pattern of Atkinson.[4]

References

[1] W. P. L. Carter, A. C. Lloyd, J. L. Sprung, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **11**, 45 (1979).

[2] R. A. Cox, K. F. Patrick, and S. A. Chant, Environ. Sci. Technol. **15**, 587 (1981).

[3] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **85**, 2698 (1981).

[4] R. Atkinson, Int. J. Chem. Kinet. **29**, 99 (1997).

[5] A. C. Baldwin, J. R. Barker, D. M. Golden, and D. G. Hendry, J. Phys. Chem. **81**, 2483 (1977).

$R_1(R_2)CHO + O_2 \rightarrow R_1COR_2 + HO_2$ or $\rightarrow$ products (1)

$R_1(R_2)CHO + M \rightarrow R_1CHO + R_2 + M$ (R = H, alkyl or substituted alkyl) (2)

Rate coefficient data

Reactions		$k_1 \cdot k_2^{-1}$/ cm^3 molecule^{-1}	Temp./K	Reference	Technique/Comments
$CH_3OCH_2O+O_2 \rightarrow CH_3OCHO+HO_2$	(1)	$k_1[O_2] \sim k_2$ (1 bar, air)	295	Jenkin *et al.*, 1993[1]	RR (a)
$CH_3OCH_2O+M \rightarrow CH_3OCHO+H+M$	(2)				
$CH_3COCH_2O+O_2 \rightarrow CH_3OCHO+HO_2$	(1)	$k_1[O_2] \ll k_2$ (1 bar, air)	298	Jenkin *et al.*, 1993[2]	RR (b)
$CH_3COCH_2O+M \rightarrow CH_3CO+HCHO+M$	(2)	$k_1[O_2] \ll k_2$ (1 bar, air)	298	Bridier *et al.*, 1993[3]	RR (c)

Comments

(a) Steady-state photolyses of Cl_2–CH_3OCH_3–O_2–N_2 mixtures at pressures of 13–1000 mbar (10–760 Torr) with long-path FTIR analyses, and molecular modulation studies of similar reactant mixtures with UV absorption monitoring of $CH_3OCH_2O_2$ radicals. In both systems, kinetic treatments indicate that reactions (1) and (2) were competing under the conditions of the experiments.

(b) Steady-state photolyses of Cl_2–CH_3COCH_3–O_2–N_2 mixtures at 930 mbar (700 Torr) with long-path FTIR and long-path UV visible diode array spectroscopy analyses of products. Data indicate that reaction (2) predominated over reaction (1) under the conditions of the experiments.

(c) Flash photolysis of Cl_2–CH_3COCH_3–air mixtures at 1 bar pressure with UV absorption monitoring of $CH_3COCH_2O_2$ radicals. Data indicate that reaction (2) predominated over reaction (1) under the conditions of the experiments.

Preferred Values

No quantitative recommendations.

Comments on Preferred Values

Although the results listed above for the reactions of the CH_3OCH_2O and CH_3COCH_2O radicals are not quantitative, for the purposes of atmospheric modeling studies it is recommended that the above qualitative information on the ratios k_1/k_2 be used to decide if one or the other of the alkoxy radical reaction pathways predominates, or if both pathways should be considered.

References

[1] M. E. Jenkin, G. D. Hayman, T. J. Wallington, M. D. Hurley, J. C. Ball, O. J. Nielsen, and T. Ellermann, J. Phys. Chem. 97, 11712 (1993).

[2] M. E. Jenkin, R. A. Cox, M. Emrich, and G. K. Moortgat, J. Chem. Soc. Faraday Trans. 89, 2983 (1993).

[3] I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. 89, 2993 (1993).

$CH_3CH(O)CH_2CH_3 + M \rightarrow CH_3CHO + C_2H_5 + M$ (1)

$\rightarrow CH_3 + C_2H_5CHO + M$ (2)

$\Delta H^\circ(1) = 24.6$ kJ·mol^{-1}

$\Delta H^\circ(2) = 28.5$ kJ·mol^{-1}

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$k_1 = 6.3\times10^{14}\exp(-7700/T)$	440–471	Batt and McCulloch, 1976[1]	S-GC (a)
$k_1 = 3.8\times10^{3}$	298*		
$k_1 = 2.5\times10^{4}$	303	Carter *et al.*, 1979[2]	S-GC (b)
$k_1 = 2.1\times10^{4}$	296	Cox, Patrick, and Chant, 1981[3]	S-GC (c)
$k_1 = 6.3\times10^{13}\exp(-7600/T)$	363–503	Heiss *et al.*, 1991[4]	F-TLC/
$k_1 = 5.3\times10^{2}$	298*		HPLC (d)
Branching Ratios			
$k_1/k_2 = 0.59\exp(1350/T)$	399–493	Drew, Kerr, and Olive, 1985[5]	S-GC (e)
$k_1/k_2 = 55$	298*		
Reviews and Evaluations			
$k_1 = 2\times10^{14}\exp(-7200/T)$	440–471	Atkinson, 1997[6]	(f)

Comments

(a) Pyrolysis of 2-butyl nitrite in the presence of NO at pressures of ~1 bar (~760 Torr) in a static system. End-product analysis of CH_3CHO by GC. Results were derived relative to the reaction $2\text{-}C_4H_9O + NO \rightarrow 2\text{-}C_4H_9ONO$ for which a value of $k = 4.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} was taken, independent of temperature.

(b) Smog chamber photolysis of $n\text{-}C_4H_{10}\text{–}NO_x$–air mixtures at 1 bar pressure. End-product analysis of CH_3CHO and $CH_3COC_2H_5$ by GC yielded $k_1/k(2\text{-}C_4H_9O + O_2) = 3.15\times10^{18}$ molecule cm^{-3}. The above value of k_1 was obtained taking $k = 8\times10^{-15}$ cm^3 molecule^{-1} s^{-1} for the reference reaction $2\text{-}C_4H_9O + O_2 \rightarrow CH_3COC_2H_5 + HO_2$ (see Ref. 6).

(c) Similar experiments as in comment (b) with $n\text{-}C_4H_{10}$–HONO–air mixtures yielding $k_1/k(2\text{-}C_4H_9O + O_2) = (2.60\pm0.35)\times10^{18}$ molecule cm^{-3}. The above value of k_1 was obtained taking $k = 8\times10^{-15}$ cm^3 molecule^{-1} s^{-1} for the reference reaction $2\text{-}C_4H_9O + O_2 \rightarrow CH_3COC_2H_5 + HO_2$ (see Ref. 6).

(d) Pyrolysis of $(2\text{-}C_4H_7O)_2$ in a stream of $O_2\text{–}N_2$ with end-product analyses. Rate data derived from a computer simulation of yields of CH_3CHO and $CH_3COC_2H_5$ and assuming that $k = 2.6\times10^{-14}\exp(-100/T)$ cm^3 molecule^{-1} s^{-1} for the competing reaction $2\text{-}C_4H_9O + O_2 \rightarrow CH_3COC_2H_5 + HO_2$.

(e) Static thermal generation of radicals from $F + 2\text{-}C_4H_9OH$ with end-product analyses of CH_3CHO and C_2H_5CHO by GC.

(f) Evaluation of reactions of RO radicals. The data of Batt and McCulloch[1] for k_1 were recalculated on the basis of $k_\infty(RO + NO) = 2.3\times10^{-11}\exp(150/T)$ cm^3 molecule^{-1} s^{-1} for the reference reaction $2\text{-}C_4H_9O + NO \rightarrow 2\text{-}C_4H_9ONO$ and by assuming that for all RO decomposition reactions $A = 2\times10^{14}d$ s^{-1}, where d is the reaction path degeneracy.

Preferred Values

$k_1 = 2.2\times10^{4}$ s^{-1} at 298 K and 1 bar pressure.

$k_1 = 2\times10^{14}\exp(-6830/T)$ s^{-1} over the temperature range 300–500 K and 1 bar pressure.

Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.
$\Delta(E_1/R) = \pm 500$ K.

Comments on Preferred Values

The preferred 298 K value is based on the measured ratios of k/k(2-butoxy+O_2) of Carter *et al.*[2] and Cox *et al.*,[3] using a rate coefficient of k(2-butoxy+O_2)$=8\times10^{-15}$ cm^3 molecule^{-1} s^{-1} to place the rate coefficient ratio on an absolute basis. The temperature dependence is derived assuming a pre-exponential factor of $A=2\times10^{14}$ s^{-1} with E/R calculated to fit the 298 K value of k_1. The effect of pressure on the value of k_1 has not been reported, but it is to be expected that at 1 bar pressure the value of k_1 is close to the high-pressure limit.

Although the branching ratio (k_1/k_2) reported by Drew *et al.*[5] seems reasonable, it requires further confirmation before a recommendation can be made. None of the othe studies[1–3] of the decomposition of the 2-C_4H_9O radicals ha reported C_2H_5CHO as a product of the decomposition reac tion, and it is possible that the radical generation system o Drew *et al.*[5] was more complicated than they suggested.

References

[1] L. Batt and R. D. McCulloch, Int. J. Chem. Kinet. **8**, 911 (1976).
[2] W. P. L. Carter, A. C. Lloyd, J. L. Sprung, and J. N. Pitts, Jr., Int. J Chem. Kinet. **11**, 45 (1979).
[3] R. A. Cox, K. F. Patrick, and S. A. Chant, Environ. Sci. Technol. **15**, 58 (1981).
[4] A. Heiss, J. Tardieu De Maleissye, V. Viossat, K. A. Sahetchian, and I. G Pitts, Int. J. Chem. Kinet. **23**, 607 (1991).
[5] R. M. Drew, J. A. Kerr, and J. Olive, Int. J. Chem. Kinet. **17**, 167 (1985)
[6] R. Atkinson, Int. J. Chem. Kinet. **29**, 99 (1997).

$CH_3 + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.1\times10^{-12}\exp[-(210\pm84)/T]$	243–384	Ogryzlo, Paltenghi, and Bayes 1991;[1]	FP-MS (a)
$(2.53\pm0.54)\times10^{-12}$	298	Paltenghi, Ogryzlo, and Bayes, 1984[2]	
Reviews and Evaluations			
$5.4\times10^{-12}\exp(-220/T)$	240–390	NASA, 1997[3]	(b)
$5.1\times10^{-12}\exp(-210/T)$	240–400	IUPAC, 1997[4]	(c)

Comments

(a) Flash photolysis of CH_3NO_2 at 193 nm in a flow system with He carrier gas at pressures of ~2.7 mbar (~2 Torr). [CH_3] was monitored by photoionization MS under pseudofirst-order conditions; no product analyses. The original data[1] were revised[2] on the basis of a correction for the pressure drop along the flow tube between the reaction vessel and the manometer.
(b) Based on data of Paltenghi *et al.*[2]
(c) See Comments on Preferred Values.

Preferred Values

$k=2.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=5.1\times10^{-12}\exp(-210/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values are based on the revised calculations by Paltenghi *et al.*[2] of the earlier data of Ogryzlo *et al.*,[1] and are identical to those in our previous evaluation, IUPAC, 1997.[4]

References

[1] E. A. Ogryzlo, R. Paltenghi, and K. D. Bayes, Int. J. Chem. Kinet. **13**, 667 (1981).
[2] R. Paltenghi, E. A. Ogryzlo, and K. D. Bayes, J. Phys. Chem. **88**, 2595 (1984).
[3] NASA Evaluation No. 12, 1997 (see references in Introduction).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3O + NO + M \rightarrow CH_3ONO + M$ (1)

$CH_3O + NO \rightarrow HCHO + HNO$ (2)

$\Delta H^\circ(1) = -172.7$ kJ·mol^{-1}
$\Delta H^\circ(2) = -103.1$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_{01}/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.35×10^{-29} $(T/298)^{-3.8}$ [Ar]	296–573	Frost and Smith, 1990[1]	PLF-LIF (a)
1.8×10^{-29} $(T/300)^{-3.2}$ [Ar]	220–473	McCaulley *et al.*, 1990[2]	DF-LIF (b)
Reviews and Evaluations			
1.4×10^{-29} $(T/300)^{-3.8}$ [air]	200–300	NASA, 1997[3]	(c)
1.6×10^{-29} $(T/300)^{-3.5}$ [air]	200–400	IUPAC, 1997[4]	(d)

Comments

(a) Rate coefficients were measured up to 165 mbar of Ar or CF_4 diluent. Evaluation of the chemical activation system $CH_3O+NO \rightarrow CH_3ONO^*$, $CH_3ONO^*+M \rightarrow CH_3ONO+M$, and $CH_3ONO^* \rightarrow HCHO+HNO$ were carried out using an extended Lindemann–Hinshelwood mechanism. At low pressures the disproportionation reaction $CH_3O+NO \rightarrow HCHO+HNO$ dominates ($k_{02} = 5.0 \times 10^{-12}(T/298)^{-0.6}$ cm^3 molecule^{-1} s^{-1}). Assuming that reactions (1) and (2) involve the same intermediate complex, k_2 is expected to decrease with increasing pressure following the relationship $k_2 = k_{02}k_1/k_{01}$.

(b) Measurements were made over the pressure range 1–6.6 mbar in He or Ar. The disproportionation reaction $CH_3O+NO \rightarrow HCHO+HNO$ was measured by molecular beam MS ($k_2 = 1.3 \times 10^{-12}$ exp$(250/T)$ cm^3 molecule^{-1} s^{-1}).

(c) Based on the results of Frost and Smith[1] for M=Ar.

(d) See Comments on Preferred Values.

Preferred Values

$k_{01} = 1.6 \times 10^{-29}(T/300)^{-3.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

$k_{02} = 4 \times 10^{-12}(T/300)^{-0.7}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_{01} = \pm 0.1$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred rate coefficient values are based on the data of Frost and Smith[1] and McCaulley *et al.*[2] and are identical to those in our previous evaluation, IUPAC, 1997.[4] The recently reported k_{01} values of Ohmori *et al.*[5] for $M=N_2$ at 296 K are a factor of 3.7 lower than previously recommended. The cause of this difference is not clear but it may be due to a different separation of k_1 and k_2.

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.1×10^{-11}	440–473	Batt, Milne, and McCulloch, 1977[6]	(a)
$(2.08\pm0.12)\times10^{-11}$	298	Sanders *et al.*, 1980[7]	(b)
1.4×10^{-11}	298	Zellner, 1987[8]	PLP-AS (c)
$3.6\times10^{-11}\ (T/298)^{-0.6}$	296–573	Frost and Smith, 1990[1]	PLF-LIF (d)
$(2.45\pm0.31)\times10^{-11}$	300	Dóbé *et al.*, 1994[9]	DF-LIF (e)
Reviews and Evaluations			
$3.6\times10^{-11}\ (T/300)^{-0.6}$	200–300	NASA, 1997[3]	(f)
$3.6\times10^{-11}\ (T/300)^{-0.6}$	200–400	IUPAC, 1997[4]	(g)

Comments

(a) Thermal decomposition of methyl nitrite in the presence of NO and $(CH_3)_3CH$. Combination of these data with the equilibrium constant gives the value indicated. For the second channel, $k(CH_3O+NO\rightarrow CH_2O+HNO)/k_\infty(CH_3O+NO\rightarrow CH_3ONO)\simeq0.17$ was estimated.

(b) Photolysis of methyl nitrite at 266 nm with CH_3O detection by LIF at He pressure of 13–66 mbar. HNO as a reaction product was also detected by LIF; however, no absolute estimate of its yield could be made.

(c) Falloff curve was measured over the range 5–500 mbar. Extrapolations carried out using $F_c=0.6$.

(d) See comment (a) for k_0.

(e) CH_3O radicals and HCHO from reaction (2) detected by LIF. The branching ratio for HCHO formation varied between 0.84 and 0.26 over the pressure range 1–11 mbar.

(f) See comment (c) for k_0.

(g) See Comments on Preferred Values.

Preferred Values

$k_1=2.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_2=2.7\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_{\infty 1}=3.6\times10^{-11}(T/300)^{-0.6}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta\log k_{\infty 1}=\pm0.5$ at 298 K.

$\Delta n=\pm0.5$.

Comments on Preferred Values

The recommended value is from Ref. 1. Because this has been evaluated with $F_c=1$, an increase of $k_{\infty 1}$ is expected when an analysis with a smaller, more realistic value of F_c is done. The preferred values are identical with our previous evaluation, IUPAC, 1997[4] and are consistent with the results of Ohmori *et al.*[5] and the more recent results of Dóbé *et al.*[9] The decrease of k_2 with increasing pressure is represented in the form $k_2=k_{02}k_1/k_{01}$, following the assumption of a common intermediate of reactions (1) and (2) from Ref. 1. Accordingly, the given value of k_2 at 1 bar was estimated. Batt[10] cites a rate coefficient ratio of $k_2/k_1<0.05$ from a study at 433–473 K, consistent with our preferred values.

References

[1] M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1757 (1990).
[2] J. A. McCaulley, A. M. Moyle, M. F. Golde, S. M. Anderson, and F. Kaufman, J. Chem. Soc. Faraday Trans. **86**, 4001 (1990).
[3] NASA Evaluation No. 12, 1997 (see references in Introduction).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).
[5] K. Ohmori, K. Yamasaki, and H. Matsui, Bull. Chem. Soc. Jpn. **66**, 51 (1993).
[6] L. Batt, R. T. Milne, and R. D. McCulloch, Int. J. Chem. Kinet. **9**, 567 (1977).
[7] N. Sanders, J. E. Butler, L. R. Pasternack, and J. R. McDonald, Chem. Phys. **48**, 203 (1980).
[8] R. Zellner, J. Chim. Phys. **84**, 403 (1987).
[9] S. Dóbé, G. Lendvay, I. Szilagyi, and T. Bérces, Int. J. Chem. Kinet. **26**, 887 (1994).
[10] L. Batt, Int. Rev. Phys. Chem. **6**, 53 (1987).

$$C_2H_5O + NO + M \rightarrow C_2H_5ONO + M \quad (1)$$

$$C_2H_5O + NO \rightarrow CH_3CHO + HNO \quad (2)$$

$\Delta H°(1) = -178.5$ kJ·mol^{-1}
$\Delta H°(2) = -127.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_{01} /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.2\pm1.2)\times10^{-28}$ [He]	298	Daële *et al.*, 1995[1]	(a)
Reviews and Evaluations			
2.8×10^{-27} $(T/300)^{-4.0}$ [air]	200–300	NASA, 1997[2]	(b)

Comments

(a) Discharge-flow technique coupled to LIF and MS analyses. C_2H_5O radicals were generated by the reaction of F atoms with C_2H_5OH. Measurements were carried out at 0.7, 1.3, and 2.6 mbar. The rate coefficient k_{01} was obtained from a Lindemann–Hinshelwood analysis, assuming identical intermediates in reactions (1) and (2), and $k_{02}=(1.1\pm0.5)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} was derived.

(b) Based on the data of Daële *et al.*[1] in He scaled to N_2, with an expression summing the bimolecular and termolecular channels. The temperature dependence was estimated.

Preferred Values

$k_{01}=2.2\times10^{-28}(T/300)^{-3.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

$k_{02}=1.1\times10^{-11}(T/300)^{-0.7}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_{01} = \pm0.3$ at 298 K.
$\Delta \log k_{02} = \pm0.5$ at 298 K.
$\Delta n = \pm0.5$.

Comments on Preferred Values

The preferred values are from Daële *et al.*,[1] assuming that reactions (1) and (2) have a common intermediate. We also assume equal values of k_{01} for He and N_2 as third bodies in contrast to the evaluation by NASA;[2] in addition, similar temperature coefficients of k_{01} and k_{02} as for the reaction CH_3O+NO (see this evaluation) are adopted. In contrast to the simple Lindemann-Hinshelwood evaluation of Ref. 1 corresponding to $F_c=1$, we use $F_c=0.6$ for a construction of the falloff curve.

High-pressure rate coefficients

Rate coefficient data

$k_{\infty1}$ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.4\pm0.4)\times10^{-11}$	298	Frost and Smith, 1990[3]	PLP-LIF (a)
$(3.1\pm0.8)\times10^{-11}$	298	Daële *et al.*, 1995[1]	(b)
Reviews and Evaluations			
5.0×10^{-11} $(T/300)^{-1.0}$	200–300	NASA, 1997[2]	(c)
4.4×10^{-11}	200–300	IUPAC, 1997[4]	(d)

Comments

(a) The rate coefficient $k_{\infty1}$ is found to be the same in the presence of 20 and 130 mbar of Ar.

(b) See comment (a) for k_0.

(c) Based on the rate data of Frost and Smith.[3] The temperature dependence was estimated.

(d) Based on the measurements of Frost and Smith.[3] The value of k_2 was estimated from the preferred value of $k_{\infty 1}$ and the ratio $k_2/k_{\infty 1}=0.3$.[5]

Preferred Values

$k_1=4.0\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_2=8\times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_{\infty 1}=4.4\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_{\infty 1}=\pm 0.3$ at 298 K.

$\Delta n=\pm 0.5$.

Comments on Preferred Values

The preferred values of $k_{\infty 1}$ are from Ref. 3. Assuming common intermediates for reactions (1) and (2),[3] such as for the reaction CH_3O+NO (see this evaluation), k_2 is assumed to decrease with increasing pressure following $k_2=k_{02}k_1/k_{01}$. For the falloff curve of reaction (1), $F_c=0.6$ is chosen.

References

[1] V. Daële, A. Ray, I. Vassalli, G. Poulet, and G. LeBras, Int. J. Chem. Kinet. **27**, 1121 (1995).

[2] NASA Evaluation No. 12, 1997 (see references in Introduction).

[3] M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1757 (1990).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

[5] G. Baker and R. Shaw, J. Chem. Soc. A, 6965 (1965).

$i\text{-}C_3H_7O + NO + M \rightarrow i\text{-}C_3H_7ONO + M$ (1)

$i\text{-}C_3H_7O + NO \rightarrow CH_3COCH_3 + HNO$ (2)

$\Delta H^\circ(2)=-142.2$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
3.4×10^{-11}	298	Balla, Nelson, and McDonald, 1985[1]	PLP-LIF (a)
Reviews and Evaluations			
3.4×10^{-11}	200–300	IUPAC, 1997[2]	(b)
$k_2=6.5\times 10^{-12}$	300		

Comments

(a) No pressure dependence of the rate coefficient was observed over the range 1.3–6 mbar. The small negative temperature dependence [$k=1.2\times 10^{-11}\exp(310/T)$ cm^3 molecule^{-1} s^{-1}] observed over the range 298–383 K may be attributed to falloff effects.

(b) Based on the data of Balla *et al.*[1] The value of k_2 was derived from the preferred $k_{\infty 1}$ and the ratio $k_2/k_1=0.19\pm 0.03$.[3]

Preferred Values

$k_1\approx k_{\infty 1}$ at 298 K and 1 bar of air.

$k_{\infty 1}=3.4\times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

$k_2=6.5\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 27–270 mbar pressure.

Reliability

$\Delta \log k_{\infty 1}=\pm 0.3$ at 298 K.

$\Delta n=\pm 0.5$.

$\Delta \log k_2=\pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred value of $k_{\infty 1}$ is based on the study of Balla *et al.*[1] and is identical to that in our previous evaluation, IUPAC, 1997.[2] The value of k_2 is obtained from the preferred $k_{\infty 1}$ and the rate coefficient ratio $k_2/k_1=0.19\pm 0.03$ (independent of temperature) cited in Ref. 3. k_2 probably decreases with increasing pressure as reaction (1) and (2) involve the same intermediate.

References

[1] R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **99**, 323 (1985).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

[3] L. Batt and R. T. Milne, Int. J. Chem. Kinet. **9**, 141 (1977).

$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M$ (1)

$CH_3O + NO_2 \rightarrow HCHO + HONO$ (2)

$\Delta H^\circ(1) = -171.5$ kJ·mol^{-1}
$\Delta H^\circ(2) = -238.5$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_{01}/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.6×10^{-29} $(T/300)^{-4.5}$ [He]	220–473	McCaulley *et al.*, 1985[1]	DF-LIF (a)
$(5.2\pm1.9)\times10^{-29}$ [He]	298	Frost and Smith, 1990[2]	PLP-LIF (b)
$(9.0\pm1.9)\times10^{-29}$ [Ar]	298		
$(11\pm3)\times10^{-29}$ [CF_4]	298		
$(4.9\pm1.2)\times10^{-29}$ [Ar]	390		
$(5.3\pm0.2)\times10^{-29}$ [He]	298	Biggs *et al.*, 1993[3]	DF-LIF (c)
Reviews and Evaluations			
1.1×10^{-28} $(T/300)^{-4.0}$ [air]	200–300	NASA, 1997[4]	(d)
2.8×10^{-29} $(T/300)^{-4.5}$ [N_2]	200–400	IUPAC, 1997[5]	(e)

Comments

(a) CH_3O radicals were produced by IR laser dissociation of $C_6F_5OCH_3$ to yield CH_3, followed by $CH_3+NO_2 \rightarrow CH_3O+NO$. Pressure range 0.8–5 mbar. Direct measurements of the branching ratio k_1/k_2 were not possible. A separation was performed by assuming that reaction (1) was in the low pressure limit.

(b) Pulsed laser photolysis of CH_3ONO–NO mixtures at 266 nm. Rate coefficients were measured over the pressure ranges 40–130 mbar of He, 8–130 mbar of Ar, and 40–100 mbar of CF_4. Falloff curves were fitted to the experimental data using the F_c values of 0.41, 0.44, and 0.48 for He, Ar, and CF_4, respectively. The recombination reaction (1) appears to dominate over reaction (2).

(c) Pressures of He varied from 1.3 to 13 mbar. Extrapolations were performed using $F_c=0.6$; an RRKM analysis was also done. A value $k_{01}=5.9\times10^{-29}$ [He] cm^3 molecule^{-1} s^{-1} was obtained.

(d) Based on the measurements of Ref. 2. The temperature dependence was estimated.

(e) Based on the uncorrected results from Ref. 2.

Preferred Values

$k_{01}=9.0\times10^{-29}(T/300)^{-4.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_{01} = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The agreement between the studies of Refs. 2 and 3 appears satisfactory, in particular if the different ways of treating the falloff curve are taken into account. We assume similar values of k_{01} for M=Ar and N_2. Falloff curves are constructed with $F_c=0.44$ at 300 K such as chosen in Ref. 2. Reaction (2) appears to play only a minor role at pressures above 10 mbar.

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comment
Absolute Rate Coefficients			
$(2.0\pm0.4)\times10^{-11}$	295	Frost and Smith, 1990[2]	LP-LIF (a)
Relative Rate Coefficients			
1.5×10^{-11}	298	Wiebe *et al.*, 1973[6]	(b)
$(1.0\pm0.5)\times10^{-11}$	392–420	Batt and Rattray, 1979[7]	(c)
$(1.4\pm0.1)\times10^{-11}$	298	Biggs *et al.*, 1993[3]	DF-LIF (d)
Branching Ratios			
$k_1/k=0.92\pm0.08$	298	Wiebe *et al.*, 1973[6]	(e)
$k_2/k_1=\leq0.05$	384–424	Batt and Rattray, 1979[7]	(f)
Reviews and Evaluations			
$1.6\times10^{-11}\,(T/300)^{-1.0}$	200–300	NASA, 1997[4]	(g)
2.0×10^{-11}	200–400	IUPAC, 1997[5]	(h)

Comments

(a) See comment (b) for k_0.

(b) Steady-state photolysis of CH_3ONO in the presence of $NO-O_2$ and $NO-NO_2-N_2$ mixtures at 10–500 mbar. Relative rate coefficients were derived from $\Phi(CH_3ONO_2)$, with $k(CH_3O+NO)/k=1.3$ at 298 K. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(CH_3O+NO\rightarrow CH_3ONO)=2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 200–400 K (CODATA, 1984[8]).

(c) Static reaction vessel, CH_3O formed from pyrolysis of CH_3OOCH_3 in the presence of $NO-NO_2-CF_4$ at a total pressure of 675 mbar. Relative rate coefficients were determined from end-product analysis of CH_3ONO and CH_3ONO_2(GC). $k(CH_3O+NO\rightarrow CH_3ONO)/k=2.03\pm0.47$ was obtained over the range 392–420 K. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(CH_3O+NO\rightarrow CH_3ONO)=2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 200–400 K (CODATA, 1984[8]). k_1/k_2 was determined from pyrolysis of CH_3OOCH_3 in the presence of NO_2 and N_2 and shown to be pressure dependent.

(d) See comment (c) for k_0. An RRKM extrapolation leads to the value $k_\infty=2.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(e)–(f) See comments (b) and (c) respectively, for k_∞.

(g)–(h) See comments (d) and (e) for k_0.

Preferred Values

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

$k_\infty=1.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

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

$\Delta n=\pm0.5$.

Comments on Preferred Values

The preferred $k_{\infty 1}$ value based on Ref. 2 appears consistent with the values for related reactions $RO+NO+M\rightarrow RONO+M$ (with $R=CH_3$, C_2H_5, i-C_3H_7, see data sheets, this evaluation). Falloff curves are constructed with $F_c=0.44$ from Ref. 2. Reaction (2) appears to be only of minor importance.[1,6,7] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

References

[1] J. A. McCaulley, S. M. Anderson, J. B. Jeffries, and F. Kaufman, Chem. Phys. Lett. **115**, 180 (1985).

[2] M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1751 (1990); **89**, 4251 (1993) (corrigendum).

[3] P. Biggs, C. E. Canosa-Mas, J.-M. Fracheboud, A. D. Parr, D. E. Shallcross, R. P. Wayne, and F. Caralp, J. Chem. Soc. Faraday Trans. **89**, 4163 (1993).

[4] NASA Evaluation No. 12, 1997 (see references in Introduction).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

[6] H. A. Wiebe, A. Villa, T. M. Hellman, and J. Heicklen, J. Am. Chem. Soc. **95**, 7 (1973).

[7] L. Batt and G. N. Rattray, Int. J. Chem. Kinet. **11**, 1183 (1979).

[8] CODATA, Supplement II, 1984 (see references in Introduction).

$C_2H_5O + NO_2 + M \rightarrow C_2H_5ONO_2 + M$ (1)

$C_2H_5O + NO_2 \rightarrow CH_3CHO + HONO$ (2)

$\Delta H°(1) = -171.7$ kJ·mol^{-1}
$\Delta H°(2) = -263.0$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.8\pm0.3)\times10^{-11}$	295	Frost and Smith, 1990[1]	PLP-LIF (a)
Reviews and Evaluations			
2.8×10^{-11} $(T/300)^{-1.0}$	200–300	NASA, 1997[2]	(b)
2.8×10^{-11}	200–300	IUPAC, 1997[3]	(c)

Comments

(a) The same rate coefficients were measured in the presence of 2 or 130 mbar of He.
(b) Based on the measurements of Ref. 1.
(c) See Comments on Preferred Values.

Preferred Values

$k_{\infty 1} = 2.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_{\infty 1} = \pm0.3$ at 298 K.
$\Delta n = \pm0.5$.

Comments on Preferred Values

The value of $k_{\infty 1}$ is based on the data of Frost and Smith,[1] and appears consistent with values for related reactions such as $RO+NO+M\rightarrow RONO+M$ (with $M=CH_3$, C_2H_5, and i-C_3H_7) or $CH_3O+NO_2+M\rightarrow CH_3ONO_2+M$ (see this evaluation). Reaction (2) appears to be of minor importance, with a rate coefficient ratio of $k_2/k_1 = 0.1\pm0.01$ at ~450 K being cited by Batt.[4] The preferred value for k_∞ is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] M. L. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1751 (1990).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
[3] IUPAC Supplement V, 1997 (see references in Introduction).
[4] L. Batt, Int. Rev. Phys. Chem. **6**, 53 (1987).

$1\text{-}C_3H_7O + NO_2 + M \rightarrow 1\text{-}C_3H_7ONO_2 + M$ (1)

$1\text{-}C_3H_7O + NO_2 \rightarrow CH_3CH_2CHO + HONO$ (2)

$\Delta H°(1) = -165.9$ kJ·mol^{-1}
$\Delta H°(2) = -258.7$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.6\pm0.4)\times10^{-11}$	296	Mund, Fockenberg, and Zellner, 1998[1]	PLP-LIF (a)

Comments

(a) The rate coefficient was observed to be independent of total pressure over the range 6.7–53 mbar.

Preferred Values

$k_{\infty 1} = 3.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of Mund *et al.*[1] with expanded uncertainty limits. The rate coefficient is of a similar magnitude to other RO+NO$_2$ reactions (see data sheets in this evaluation for CH$_3$O+NO$_2$, C$_2$H$_5$O+NO$_2$, and 2-C$_3$H$_7$O+NO$_2$).

References

[1] C. Mund, Ch. Fockenberg, and R. Zellner, Ber. Bunsenges. Phys. Chem. **102**, 709 (1998).

$2\text{-}C_3H_7O + NO_2 + M \rightarrow 2\text{-}C_3H_7ONO_2 + M$ (1)

$2\text{-}C_3H_7O + NO_2 \rightarrow CH_3C(O)CH_3 + HONO$ (2)

$\Delta H°(1) = -171.7$ kJ·mol^{-1}

$\Delta H°(2) = -277.6$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
3.5×10^{-11}	298	Balla, Nelson, and McDonald, 1985[1]	PLP-LIF (a)
$(3.3 \pm 0.3) \times 10^{-11}$	296	Mund, Fockenberg, and Zellner, 1998[2]	PLP-LIF (b)
Reviews and Evaluations			
3.5×10^{-11}	200–300	IUPAC, 1997[3]	(c)

Comments

(a) By extrapolation to zero laser power, a rate coefficient of $k_{\infty 1} = 1.5 \times 10^{-11} \exp[(250 \pm 200)/T]$ cm^3 molecule^{-1} s^{-1} was derived from measurements over the temperature range 295–384 K. No pressure dependence was observed between 1.3 and 13 mbar.

(b) The measured rate coefficient was observed to be independent of total pressure over the range 6.7–106 mbar.

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

Comments on Preferred Values

The recommendation is based on the data of Balla *et al.*[1] and Mund *et al.*[2] The value of $k_{\infty 1}$ is consistent with other related reactions such as RO+NO+M→RONO+M and RO+NO$_2$+M→RONO$_2$+M (with R=CH$_3$, C$_2$H$_5$, *i*-C$_3$H$_7$, see this evaluation). The preferred values are identical to those of our previous evaluation, IUPAC, 1997.[3] It is estimated that $k_2/k_{\infty 1} < 0.2$. Batt[4] cites a rate coefficient ratio of $k_2/k_1 = 0.027 \pm 0.006$ at ~450 K, indicating that reaction (2) is of negligible importance under atmospheric conditions.

Preferred Values

$k_{\infty 1} = 3.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.2$ at 298 K.

$\Delta n = \pm 0.5$.

References

[1] R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **99**, 323 (1985).

[2] Ch. Mund, Ch. Fockenberg, and R. Zellner, Ber. Bunsenges. Phys. Chem. **102**, 709 (1998).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

[4] L. Batt, Int. Rev. Phys. Chem. **6**, 53 (1987).

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

$\Delta H^\circ = -50.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(11.2 \pm 1.4) \times 10^{-12}$	298	Masaki, Tsunashima, and Washida, 1994[1]	DF-MS (a)
$2.8 \times 10^{-12} \exp[(285 \pm 60)/T]$	199–429	Villalta, Huey, and Howard, 1995[2]	F-CIMS (b)
$(7.5 \pm 1.3) \times 10^{-12}$	298		
$(7.5 \pm 1.0) \times 10^{-12}$	298	Helleis, Moortgat, and Crowley, 1996[3]	DF-MS (c)
Reviews and Evaluations			
$3.0 \times 10^{-12} \exp(280/T)$	200–300	NASA, 1997[4]	(d)
$4.2 \times 10^{-12} \exp(180/T)$	240–360	IUPAC, 1997[5]	(e)

Comments

(a) Mass spectrometry using photoionization detection of CH_3O_2.

(b) Mass spectrometry using CI-detection of CH_3O_2 positive ions. k determined from pseudo-first order loss of CH_3O_2 in the presence of excess NO.

(c) Electron impact detection of CH_3O_2 in excess NO. Measurements using deuterated methyl peroxy gave $k(CD_3O_2+NO) = (8.6 \pm 1.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

(d) k_{298} is derived from the results of Sander and Watson,[6] Ravishankara *et al.*,[7] Cox and Tyndall,[8] Plumb *et al.*,[9] Simonaitis and Heicklen,[10] Zellner *et al.*,[11] and Villalta *et al.*[2] The temperature dependence was derived from a weighted least-squares analysis of the data of Ravishankara *et al.*,[7] Simonaitis and Heicklen,[10] and Villalta *et al.*[2]

(e) k_{298} was the mean of the data of Plumb *et al.*,[9] Cox and Tyndall,[8] Sander and Watson,[6] Ravishankara *et al.*,[7] Simonaitis and Heicklen,[10] and Zellner *et al.*,[11] and E/R was from the data of Ravishankara *et al.*[7] and Simonaitis and Heicklen.[10]

Preferred Values

$k = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.8 \times 10^{-12} \exp(285/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–430 K.

Reliability

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

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

Comments on Preferred Values

The new DF-MS data of Villalta *et al.*[2] and Helleis *et al.*[3] provide values of k_{298} which are in excellent agreement with the previous recommendations, and with improved precision. The values from Masaki *et al.*[1] are outside the range of values observed by all other reliable studies and must have an unidentified source of error. The temperature dependence of Villalta *et al.*[2] is based on a wider range than studied hitherto and with increased precision in the data. The data of Ravishankara *et al.*[7] did not show a consistent trend with temperature over the range 240–339 K $[E/R = -(86 \pm 112)$ K$]$. The higher value of $E/R = -(380 \pm 250)$ K obtained by Simonaitis and Heicklen[10] was influenced strongly by two data points at 218 K which are significantly higher than the Villalta *et al.*[2] data. The Arrhenius expression determined by Villalta *et al.*[2] gives the best representation of all relevant data and is recommended here.

The alternative reaction channel of the peroxy+NO reaction leading to the formation of alkyl nitrate has never been observed for CH_3O_2 and accounts for <1% of the overall reaction at room temperature and below.

References

[1] A. Masaki, S. Tsunashima, and N. Washida, Chem. Phys. Lett. **218**, 523 (1994).
[2] P. W. Villalta, L. G. Huey, and C. J. Howard, J. Phys. Chem. **99**, 12829 (1995).
[3] F. Helleis, C. K. Moortgat, and J. N. Crowley, J. Phys. Chem. **100**, 17846 (1996).
[4] NASA Evaluation No. 12, 1997 (see references in Introduction).
[5] IUPAC, Supplement V, 1997 (see references in Introduction).
[6] S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).
[7] A. R. Ravishankara, F. L. Eisele, N. M. Kreutter, and P. H. Wine, J. Chem. Phys. **74**, 2267 (1981).
[8] R. A. Cox and G. S. Tyndall, Chem. Phys. Lett. **65**, 357 (1979); J. Chem. Soc. Faraday Trans. 2 **76**, 153 (1980).
[9] I. C. Plumb, K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, J. Phys. Chem. **85**, 3136 (1981).
[10] R. Simonaitis and J. Heicklen, J. Phys. Chem. **85**, 2946 (1981).
[11] R. Zellner, B. Fritz, and K. Lorenz, J. Atmos. Chem. **4**, 241 (1986).

$$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2 \quad (1)$$

$$C_2H_5O_2 + NO + M \rightarrow C_2H_5ONO_2 + M \quad (2)$$

$\Delta H^\circ(1) = -43.8$ kJ·mol^{-1}
$\Delta H^\circ(2) = -215.6$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.2 \pm 1.6) \times 10^{-12}$	295	Däele *et al.*, 1995[1]	DF-MS (a)
$3.1 \times 10^{-12} \exp[(330 \pm 110)/T]$	220–355	Maricq and Szente, 1996[2]	PLP-AS (b)
$(1.0 \pm 0.15) \times 10^{-11}$	295		
$2.6 \times 10^{-12} \exp[(380 \pm 70)/T]$	207–403	Eberhard and Howard, 1996[3]	F-CIMS (c)
$(9.3 \pm 1.6) \times 10^{-12}$			
$(8.5 \pm 1.2) \times 10^{-12}$	298	Sehested, Nielsen, and Wallington, 1993[4]	PR-UVAS
$(8.9 \pm 3.0) \times 10^{-12}$	295	Plumb *et al.*, 1982[5]	DF-MS
Branching Ratio			
$k_2/k \leq 0.014$ (1 bar)	299	Atkinson *et al.*, 1982[6]	(d)
Reviews and Evaluations			
$2.6 \times 10^{-12} \exp(365/T)$	200–410	NASA, 1997[7]	(e)
8.7×10^{-12}	298	IUPAC, 1997[8]	(f)

Comments

(a) Conventional discharge flow system with LIF detection of C_2H_5O product. k determined by simulation of experimental C_2H_5O profiles.

(b) Excimer laser photolysis of Cl_2–C_2H_6–NO–O_2–N_2 mixtures. Time-resolved measurements of $C_2H_5O_2$ decay and C_2H_5ONO formation using diode array UV absorption spectroscopy, and of NO loss and NO_2 formation using diode laser absorption spectroscopy.

(c) Ethyl radicals from thermal decomposition of *n*-propyl nitrate followed by reaction of C_2H_5 decomposition fragment with O_2, or by rf discharge through C_2H_5I. Pseudo-first order kinetics with excess NO and CIMS detection of $C_2H_5O_2$ as the ethyl peroxy negative ion.

(d) GC analysis of $C_2H_5ONO_2$ product from photooxidation of C_2H_6 in Cl_2–C_2H_6–NO–air mixtures.

(e) Based on the data of Refs. 1–5.

(f) Based on the data of Plumb *et al.*[5] and Sehested *et al.*[4]

Preferred Values

$k = 9.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.5 \times 10^{-12} \exp(380/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–410 K.

$k_2/k \leq 0.014$ at 298 K and 1 bar pressure.

Reliability

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

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

Comments on Preferred Values

The new measurements[1–3] are all in excellent agreement with the earlier data of Plumb *et al.*[5] and Sehested *et al.*[4] The temperature coefficients (E/R) from the two recent studies[2,3] are in excellent agreement and confirm the emerging picture of significant negative temperature dependence for the RO_2+NO reactions.

The preferred value for k(298 K) is the mean of the results from Refs. 1–5. The expression for the temperature dependence accepts the E/R from Eberhard and Howard,[3] because this is based on a wide range of temperature and has better precision.

The branching ratio for $C_2H_5ONO_2$ formation is based on the work of Atkinson *et al.*[6]

References

[1] V. Däele, A. Ray, I. Vassalli, G. Poulet, and G. Le Bras, Int. J. Chem. Kinet. **27**, 1121 (1995).
[2] M. M. Maricq and J. J. Szente, J. Phys. Chem. **100**, 12374 (1996).
[3] J. Eberhard and C. J. Howard, Int. J. Chem. Kinet. **28**, 731 (1996).
[4] J. Sehested, O. J. Nielsen, and T. J. Wallington, Chem. Phys. Lett. **213**, 457 (1993).
[5] I. C. Plumb, K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, Int. J. Chem. Kinet. **14**, 183 (1982).
[6] R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **86**, 4563 (1982).
[7] NASA Evaluation No. 12, 1997 (see references in Introduction).
[8] IUPAC, Supplement V, 1997 (see references in Introduction).

$HOCH_2CH_2O_2 + NO \rightarrow HOCH_2CH_2O + NO_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9 \pm 4) \times 10^{-12}$	298	Becker, Geiger, and Wiesen, 1991[1]	PLP-LIF (a)
Reviews and Evaluations			
9×10^{-12}	298	Lightfoot *et al.*, 1992[2]	(b)
9×10^{-12}	298	IUPAC, 1997[3]	(b)

Comments

(a) Pulsed laser photolysis of H_2O_2 in the presence of C_2H_4–O_2–NO mixtures at a total pressure of 1 bar [(760±5) Torr]. Relative OH radical concentrations were determined as a function of time using LIF, and simulated by a mechanism consisting of 11 reactions, of which k of above reaction was the most sensitive.

(b) See Comments on Preferred Values.

Preferred Values

$k = 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The rate coefficient reported by Becker *et al.*,[1] which is recommended, is consistent with the rate coefficients of the reactions of other peroxy radicals with NO. Independent confirmation is needed to reduce the recommended error limits. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[3]

References

[1] K. H. Becker, H. Geiger, and P. Wiesen, Chem. Phys. Lett. **184**, 256 (1991).
[2] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$n\text{-}C_3H_7O_2 + NO \rightarrow n\text{-}C_3H_7O + NO_2$ (1)

$n\text{-}C_3H_7O_2 + NO + M \rightarrow n\text{-}C_3H_7ONO_2 + M$ (2)

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.9 \times 10^{-12} \exp[(350 \pm 60)/T]$	201–402	Eberhard and Howard, 1996[1]	(a)
$(9.4 \pm 1.6) \times 10^{-12}$	298		
Branching Ratios			
$k_2/k = 0.020 \pm 0.009$ (1 bar)	299	Atkinson *et al.*, 1982;[2] Carter and Atkinson, 1989[3]	(b)
Reviews and Evaluations			
5.0×10^{-12}	298	IUPAC, 1997[4]	(c)

Comments

(a) $n\text{-}C_3H_7O_2$ radicals were produced by pyrolysis of $n\text{-}C_3H_7ONO_2$ in the presence of O_2 and detected by CIMS. Pseudo-first order kinetics with excess NO.

(b) Based on yield of $n\text{-}C_3H_7ONO_2$ product from photooxidation of C_3H_8 in NO_x–air mixtures. Carter and Atkinson[3] revised the analysis of original data to provide the values quoted.

(c) Based on analogy to the reaction $i\text{-}C_3H_7O_2$+NO. The branching ratio was based on the measurements of Atkinson *et al.*[2]

Preferred Values

$k=9.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=2.9\times10^{-12}\exp(350/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–410 K.

$k_2/k=0.020$ at 298 K and 1 bar pressure.

Reliability

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

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

$\Delta\log(k_2/k)=\pm0.3$ at 298 K and 1 bar pressure.

Comments on Preferred Values

The new measurements of Eberhard and Howard[1] provide the only experimental measurements of this rate coefficient. The value of k_{298} is in line with the most recent measurements for reactions of ethyl peroxy and 2-propyl peroxy radicals with NO. The temperature coefficient supports the emerging picture of a significant negative temperature dependence of the rate coefficient for the RO_2+NO reactions. The recommendation accepts the Arrhenius expression of Eberhard and Howard,[1] and supersedes our earlier IUPAC recommendation.[4]

The preferred branching ratio for *n*-propyl nitrate formation is that measured by Atkinson *et al.*,[2] as revised by Carter and Atkinson.[3]

References

[1] J. Eberhard and C. J. Howard, Int. J. Chem. Kinet. **28**, 731 (1996).
[2] R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **86**, 4563 (1982).
[3] W. P. L. Carter and R. Atkinson, J. Atmos. Chem. **8**, 165 (1989).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$i\text{-}C_3H_7O_2 + NO \rightarrow i\text{-}C_3H_7O + NO_2$ (1)

$i\text{-}C_3H_7O_2 + NO + M \rightarrow i\text{-}C_3H_7ONO_2 + M$ (2)

$\Delta H^\circ(1)=-40.5$ kJ·mol^{-1}
$\Delta H^\circ(2)=-212.2$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.7\times10^{-12}\exp[(360\pm60)/T]$	201–401	Eberhard, Villalta, and Howard, 1996[1]	F-CIMS (a)
$(9.0\pm1.5)\times10^{-12}$	298		
$(9.1\pm1.5)\times10^{-12}$	298	Eberhard and Howard, 1996[2]	F-CIMS (b)
Branching Ratios			
$k_2/k=0.042\pm0.003$ (1 bar air)	299	Atkinson *et al.*, 1982;[3] Carter and Atkinson, 1989[4]	(c)
Reviews and Evaluations			
5.0×10^{-12}	298	IUPAC, 1997[5]	(c)

Comments

(a) $i\text{-}C_3H_7O_2$ radicals produced by reaction of O_2 with $i\text{-}C_3H_7$ radicals produced by thermal decomposition of isobutyl nitrate. $i\text{-}C_3H_7O_2$ was detected as its parent negative ion formed by reaction with O_2^-. k determined by pseudo-first order loss of $i\text{-}C_3H_7O_2$ in the presence of NO.

(b) $i\text{-}C_3H_7O_2$ produced by reaction of O_2 with $i\text{-}C_3H_7$ produced in a low frequency rf discharge through *i*-propyl iodide.

(c) Photolysis of CH_3ONO–NO–C_3H_8–air or Cl_2–NO–C_3H_8–air mixtures at a total pressure of 1 bar. The branching ratio was determined[3] from the measured yields of $i\text{-}C_3H_7ONO_2$ and the consumption of C_3H_8. Carter and Atkinson[4] have reevaluated the branching ratio, cited above, from the original data[3] on the basis of revised data for the rate coefficients of the HO radical reactions with alkanes.

(d) Based on the DF-MS study of Peeters *et al.*[6]

Preferred Values

$k=9.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=2.7\times10^{-12}\exp(360/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–410 K.

$k_2/k=0.042$ at 298 K and 1 bar pressure.

Reliability

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

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

$\Delta\log(k_2/k)=\pm0.3$ at 298 K and 1 bar pressure.

Comments on Preferred Values

The new data from Eberhard *et al.*[1,2] using improved techniques for radical generation and detection gives a rate coefficient at 298 K which is almost a factor of 2 higher than the value obtained by Peeters *et al.*,[6] and is close to the value obtained for a range of alkyl peroxy radicals at 298 K. The preferred value for k_{298} and the temperature dependence is that reported by Eberhard *et al.*,[1] which appears reliable.

The recommended branching ratio is that recalculated by Carter and Atkinson[4] based on the original data of Atkinson *et al.*,[3] and using updated data for the OH radical reactions with alkanes.

References

[1] J. Eberhard, P. W. Villalta, and C. J. Howard, J. Phys. Chem. **100**, 993 (1996).

[2] J. Eberhard and C. J. Howard, Int. J. Chem. Kinet. **28**, 731 (1996).

[3] R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **86**, 4563 (1982).

[4] W. P. L. Carter and R. Atkinson, J. Atmos. Chem. **8**, 165 (1989).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

[6] J. Peeters, J. Vertommen, and I. Langhans, Ber. Bunsenges. Phys. Chem. **96**, 431 (1992).

$CH_3C(O)O_2 + NO \rightarrow CH_3C(O)O + NO_2$

$\Delta H° = -93\ kJ\cdot mol^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.1\times10^{-12}\exp[(570\pm140)/T]$	228–354	Maricq and Szente, 1996[1]	PLP-AS (a)
$(1.4\pm0.2)\times10^{-11}$	298		
$8.1\times10^{-12}\exp[(270\pm60)/T]$	200–402	Villalta and Howard, 1996[2]	F-CIMS (b)
$(2.0\pm0.3)\times10^{-11}$	298		
$(2.0\pm0.3)\times10^{-11}$	295	Sehested *et al.*, 1998[3]	PR-A (c)
Relative Rate Coefficients			
$8.9\times10^{-12}\exp[(312\pm46)/T]$ (1 bar air)	247–298	Seefeld, Kinnison, and Kerr, 1997[4]	(d)
$(2.5\pm0.4)\times10^{-11}$ (1 bar air)	298		
$(2.19\pm0.23)\times10^{-11}$ (0.93 bar)	295	Sehested *et al.*, 1998[3]	(e)
Reviews and Evaluations			
$5.3\pm10^{-12}\exp(360/T)$	249–367	NASA, 1997[5]	(f)
2.0×10^{-11}	280–325	IUPAC, 1997[6]	(g)

Comments

(a) Pulsed laser photolysis of Cl_2–CH_3CHO–O_2–NO mixtures at 351 nm. Time-resolved absorption spectroscopy using a gated diode array for $CH_3C(O)O_2$ in the UV and using a diode laser for NO and NO_2 in the IR. Correction to k required for competing reactions of $CH_3C(O)O_2$.

(b) $CH_3C(O)O_2$ produced by thermal decomposition of peroxyacetyl nitrate and detected by CIMS through its reaction with SF_6^-. NO_2, CH_3, and CO_2 were positively identified as products implying rapid decomposition of $CH_3C(O)O$ to CH_3 and CO_2.

(c) Pulse radiolysis of CH_3CHO–O_2–CO_2–NO and CH_3CHO–O_2–SF_6–NO mixtures at 1 bar pressure. The rate coefficient was obtained from the formation of NO_2, measured by absorption at 400.5 nm.

(d) $CH_3C(O)O_2$ produced by steady-state photolysis of biacetyl in the presence of O_2. Yields of peroxyacetyl nitrate were measured as a function of the [NO]/[NO_2] ratio. Data gave $k/k(CH_3C(O)O_2+NO_2) = 2.44\pm0.18$ at 1 bar, independent of temperature over the range 247–298 K. The expression in the table is calculated using our recommended values for $k(CH_3C(O)O_2+NO_2)$ at 1 bar pressure.

(e) $CH_3C(O)O_2$ radicals were produced by photolysis of Cl_2–CH_3CHO–O_2 mixtures, and reactants and products monitored by FTIR spectroscopy. The measured rate coefficient ratio $k(CH_3C(O)O_2+NO)/k(CH_3C(O)O_2+NO_2) = 2.07\pm0.21$ at 932 mbar N_2 is placed on an absolute basis using the recommended value of $k(CH_3C(O)O_2+NO_2)$ [this evaluation].

(f) Based on data of Maricq and Szente[1] and Villalta and Howard.[2]

(g) Based on the relative rate measurements of Cox *et al.*,[7] Cox and Roffey,[8] Hendry and Kenley,[9] Kirchner *et al.*,[10] and Tuazon *et al.*[11]

Preferred Values

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

$k = 7.8\times10^{-12}\exp(300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–350 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

The new direct measurements of Villalta and Howard[2] and Sehested *et al.*[3] at 298 K are in good agreement with the value derived from the earlier relative rate data, on which the previous IUPAC recommendations[6] were based. The measurements of Maricq and Szente[1] give a value of k(298 K) approximately 30% lower than, and their temperature coefficient (E/R) is twice as large as, that of Villalta and Howard.[2] The recent relative rate study of Seefeld *et al.*[4] provided improved accuracy and an extended range to low temperatures. The values of k based on the IUPAC recommendation for the reference reaction are in good agreement with the values of Villalta and Howard[2] and Sehested *et al.*[3] The recommendation is based on the 298 K measurements of Villalta and Howard[2] and Sehested *et al.*,[3] with E/R increased slightly to take into account the larger temperature coefficient observed by Maricq and Szente[1] and Seefeld *et al.*[4] The earlier data for k, obtained relative to $k(CH_3C(O)O_2 + NO_2)$,[7–11] are generally consistent with this recommendation.

References

[1] M. M. Maricq and J. J. Szente, J. Phys. Chem. **100**, 12380 (1996).
[2] P. W. Villalta and C. J. Howard, J. Phys. Chem. **100**, 13624 (1996).
[3] J. Sehested, L. K. Christensen, T. Møgelberg, O. J. Nielsen, T. J. Wallington, A. Guschin, J. J. Orlando, and G. S. Tyndall, J. Phys. Chem. A **102**, 1779 (1998).
[4] S. Seefeld, D. J. Kinnison, and J. A. Kerr, J. Phys. Chem. A **101**, 55 (1997).
[5] NASA Evaluation No. 12, 1997 (see references in Introduction).
[6] IUPAC, Supplement V, 1997 (see references in Introduction).
[7] R. A. Cox, R. G. Derwent, P. M. Holt, and J. A. Kerr, J. Chem. Soc. Faraday Trans. **72**, 2061 (1976).
[8] R. A. Cox and M. J. Roffey, Environ. Sci. Technol. **11**, 900 (1977).
[9] D. G. Hendry and R. A. Kenley, J. Am. Chem. Soc. **99**, 3198 (1977).
[10] F. Kirchner, F. Zabel, and K. H. Becker, Ber. Bunsenges. Phys. Chem. **94**, 1379 (1990).
[11] E. C. Tuazon, W. P. L. Carter, and R. Atkinson, J. Phys. Chem. **95**, 2434 (1991).

$C_2H_5C(O)O_2 + NO \rightarrow C_2H_5C(O)O + NO_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$1.25 \times 10^{-11} \exp(240/T)$	249–302	Seefeld and Kerr, 1997[1]	(a)
$(2.8 \pm 0.4) \times 10^{-11}$	298		
Reviews and Evaluations			
2.0×10^{-11}	298	IUPAC, 1997[2]	(b)

Comments

(a) Ratio $k/k(C_2H_5C(O)O_2 + NO_2) = 2.33 \pm 0.38$, independent of temperature over the range 249–302 K. $C_2H_5C(O)O_2$ produced by photolysis of $C_2H_5C(O)Cl$ in a flow system at 1 atm pressure with analysis of $C_2H_5C(O)O_2NO_2$ by GC, as a function of the $[NO]/[NO_2]$ ratio. k calculated with $k(C_2H_5C(O)O_2 + NO_2) = k_\infty(CH_3C(O)O_2 + NO_2)$ from the present evaluation (in Arrhenius form, $k_\infty(CH_3C(O)O_2 + NO_2) = 5.4 \times 10^{-12} \exp(240/T)$ cm^3 molecule^{-1} s^{-1} over the range 250–300 K). Also showed that the above rate constant ratio was $11 \pm 13\%$ higher than the corresponding ratio for $CH_3C(O)O_2$, which is consistent with a higher rate coefficient for the $RO_2 + NO_2(+M)$ reaction for the C_3 acylperoxy radical.

(b) Based on the work of Kerr and Stocker.[3]

Preferred Values

$k = 2.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.2 \times 10^{-11} \exp(240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–310 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The rate coefficient is very similar in magnitude to the corresponding reaction of the acetylperoxy radical, for which there is very good agreement between relative rate determinations using the same technique, and direct determinations. Thus confidence can be placed in the indirect determination and the results of Seefeld and Kerr[1] form the basis for the recommendation, which supersedes that based on the earlier work of Kerr and Stocker.[3]

References

[1] S. Seefeld and J. A. Kerr, Environ. Sci. Technol. **31**, 2949 (1997).
[2] IUPAC, Supplement V, 1997 (see references in Introduction).
[3] J. A. Kerr and D. W. Stocker, J. Photochem. **28**, 475 (1985).

$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$

$\Delta H° = -88$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0 /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.33\pm0.08)\times10^{-30}$ [N_2]	298	Sander and Watson, 1980[1]	FP-AS (a)
2.2×10^{-30} $(T/300)^{-2.5}$ [N_2]	253–353	Ravishankara, Eisele, and Wine, 1980[2]	FP-AS (b)
Reviews and Evaluations			
2.5×10^{-30} $(T/298)^{-5.5}$ [N_2]	253–353	Destriau and Troe, 1990[3]	(c)
1.5×10^{-30} $(T/300)^{-4.0}$ [N_2]	200–300	NASA, 1997[4]	(d)
2.5×10^{-30} $(T/300)^{-5.5}$ [N_2]	250–350	IUPAC, 1997[5]	(e)

Comments

(a) Pressure range 70–900 mbar for the bath gases He, N_2, and SF_6. Analysis of the falloff curve was carried out with a theoretical F_c value of 0.39, in good agreement with the fitted value of $F_c = 0.4\pm0.10$.

(b) Pressure range 100–950 mbar. Analyses of the falloff curves at 253, 298, and 353 K were carried out with $F_c = 0.4$ independent of temperature.

(c) Theoretical analysis based on recombination data from Refs. 1 and 2 and dissociation data from Ref. 6. In order to extrapolate k_0, a temperature-independent value of $k_\infty = 7.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} and $F_c = 0.36$ (at 300 K) were used. The comparison of dissociation and recombination experiments led to $\Delta H° = -88.5$ kJ mol^{-1}.

(d) Based on the rate data from Refs. 1 and 2 analyzed with $F_c = 0.6$.

(e) Based on the theoretical analysis of Ref. 3, which used the experimental data of Refs. 1, 2, and 6.

Preferred Values

$k_0 = 2.5\times10^{-30}(T/300)^{-5.5}$ [N_2] cm^3 molecule^{-1} s^{-1}, over the temperature range 250–350 K.

Reliability

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

$\Delta n = \pm1$.

Comments on Preferred Values

The preferred values are based on the theoretical analysis of Ref. 3 which used the previous experimental determinations. These values are based on a theoretically determined value of $F_c = 0.36$ at 300 K. The difference between the recommendations of Refs. 4 and 5 is due to the different values of F_c used, with the analysis of Ref. 4 being based on a standard value of $F_c = 0.6$. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

High-pressure rate coefficients

Rate coefficient data

k_∞ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.0\pm1.0)\times10^{-12}$	298	Sander and Watson, 1980[1]	FP-AS (a)
7×10^{-12} $(T/298)^{-3.5}$	253–353	Ravishankara, Eisele, and Wine, 1980[2]	FP-AS (b)
Reviews and Evaluations			
7.5×10^{-12}	253–353	Destriau and Troe, 1990[3]	(c)
6.5×10^{-12} $(T/300)^{-2.0}$	200–300	NASA, 1997[4]	(d)
7.5×10^{-12}	250–350	IUPAC, 1997[5]	(e)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0. The large negative temperature coefficient is probably an artifact of the interpretation. If a larger negative temperature exponent for k_0 and a smaller F_c value at higher temperature are used, the large negative temperature exponent of k_∞ will decrease.

(c)–(e) See comments (c)–(e) for k_0.

Preferred Values

$k = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–350 K.

Reliability

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

$\Delta n = \pm 0.5$.

Comments on Preferred Values

See comments on k_0. An experimental value of $F_c = 0.36$ at 298 K appears well established. A temperature dependence of F_c must be expected, probably similar to that for $NO_2 + NO_3 \rightarrow N_2O_5$ (IUPAC, 1997[7]). Less complete information on the falloff range is obtained from the experiments by Cox and Tyndall,[8] who measured $k = 1.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 700 mbar of N_2 and 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 66 mbar of Ar at 275 K. The apparent observation of a pressure independent rate coefficient k over the range 66–760 mbar of Ar, reported by Adachi and Basco,[9] is not confirmed by Refs. 1 and 2.

References

[1] S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).
[2] A. R. Ravishankara, F. L. Eisele, and P. H. Wine, J. Chem. Phys. **73**, 3743 (1980).
[3] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[4] NASA Evaluation No. 12, 1997 (see references in Introduction).
[5] IUPAC, Supplement V, 1997 (see references in Introduction).
[6] F. Zabel, A. Reimer, K. H. Becker, and E. H. Fink, J. Phys. Chem. **93**, 5500 (1989).
[7] IUPAC, Supplement VI, 1997 (see references in Introduction).
[8] R. A. Cox and G. S. Tyndall, J. Chem. Soc. Faraday Trans. 2 **76**, 153 (1980).
[9] H. Adachi and N. Basco, Int. J. Chem. Kinet. **12**, 1 (1980).

$CH_3O_2NO_2 + M \rightarrow CH_3O_2 + NO_2 + M$

$\Delta H^\circ = 88$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$9.0 \times 10^{-5} \exp(-9694/T)$ [N_2]	248–273	Zabel *et al.*, 1989[1]	(a)
6.7×10^{-19} [N_2]	298		
Reviews and Evaluations			
5.7×10^{-19} [air]	298	NASA, 1997[2]	(b)
$9 \times 10^{-5} \exp(-9690/T)$ [N_2]	250–300	IUPAC, 1997[3]	(c)

Comments

(a) Rate of decomposition of $CH_3O_2NO_2$ followed by FTIR spectroscopy after generation in a reaction chamber, with subsequent addition of NO to scavenge CH_3O_2 radicals. Falloff curves were fitted with $F_c = 0.4$ and F_c-dependent broadening.

(b) Evaluated with the preferred rate of the reverse reaction and the equilibrium constant K_c from Ref. 2.

(c) Based on the theoretical analysis of Ref. 4 of the rate data of Ref. 1 and the reverse recombination reaction.[5,6]

Preferred Values

$k_0 = 6.8 \times 10^{-19}$ [N_2] s^{-1} at 298 K.

$k_0 = 9 \times 10^{-5} \exp(-9690/T)$ [N_2] s^{-1} over the temperature range 250–300 K.

Reliability

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

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

Comments on Preferred Values

The preferred values correspond to the data and analysis of Ref. 1. A theoretical analysis of these data and those of the reverse reaction in Ref. 4 gives an internally consistent picture (with $\Delta H° = 88.5$ kJ mol^{-1}). Slightly lower limiting rate coefficients were obtained in Ref. 7 where a value of $F_c = 0.6$ was used. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[3]

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.1\times10^{16}\exp(-10920/T)$	256–268	Bahta, Simonaitis, and Heicklen, 1982[7]	(a)
2.6	298*		
$1.1\times10^{16}\exp(-10560/T)$	248–273	Zabel *et al.*, 1989[1]	(b)
4.5	298*		
Reviews and Evaluations			
2.4	298	NASA, 1997[2]	(c)
$1.1\times10^{16}\exp(-10560/T)$	250–300	IUPAC, 1997[3]	(d)

Comments

(a) $CH_3O_2NO_2$ generated by photolysis of Cl_2 in the presence of NO_2, CH_4, and O_2. Kinetics were monitored in the presence of NO by UV absorption at 250 nm. At 460 mbar, $k = 6\times10^{15}\exp(-10620/T)$ s^{-1}. The given value of k_∞ is derived with $F_c = 0.6$. The data depend to some extent on the rate coefficient for the reaction $CH_3O_2 + NO \rightarrow CH_3O + NO_2$.

(b)–(d) See comments (a)–(c) for k_0.

Preferred Values

$k = 1.8$ s^{-1} at 298 K and 1 bar of air.

$k_\infty = 4.5$ s^{-1} at 298 K.

$k_\infty = 1.1\times10^{16}\exp(-10560/T)$ s^{-1} over the temperature range 250–300 K.

Reliability

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

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

Comments on Preferred Values

See Comments on Preferred Values of k_0.

References

[1] F. Zabel, A. Reimer, K. H. Becker, and E. H. Fink, J. Phys. Chem. **93**, 5500 (1989).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).
[4] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[5] S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).
[6] A. R. Ravishankara, F. L. Eisele, and P. H. Wine, J. Chem. Phys. **73**, 3743 (1980).
[7] A. Bahta, R. Simonaitis, and J. Heicklen, J. Phys. Chem. **86**, 1849 (1982).

$C_2H_5O_2+NO_2+M \rightarrow C_2H_5O_2NO_2+M$

$\Delta H° = -67.7$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
4.8×10^{-29} [N_2]	254	Elfers, Zabel, and Becker, 1990[1]	(a)
Reviews and Evaluations			
7.9×10^{-30} $(T/298)^{-6.2}$ [N_2]	200–300	Destriau and Troe, 1990[2]	(b)
2.2×10^{-29} [N_2]	254		
1.3×10^{-29} $(T/300)^{-6.2}$	200–300	IUPAC, 1997[3]	(c)

Comments

(a) Thermal decomposition of $C_2H_5O_2NO_2$ in a glass reaction chamber in the presence of differing initial $[NO_2]/[NO]$ ratios at total pressures of 10–1000 mbar. $C_2H_5O_2NO_2$ was prepared *in situ* by the photolysis of Cl_2–C_2H_6–O_2–NO_2–N_2 mixtures. $C_2H_5O_2NO_2$, NO_2, and NO concentrations were monitored by longpath FTIR absorption and rate coefficient ratios for the reaction of $C_2H_5O_2$ with NO and NO_2 were obtained. The reported rate coefficient for $C_2H_5O_2+NO_2$ was derived using a rate coefficient of 8.9×10^{-12} cm^3 molecule^{-1} s^{-1} for the reaction $C_2H_5O_2+NO \rightarrow C_2H_5O+NO_2$. Falloff curves were constructed based on the theoretical analysis from Ref. 2.

(b) Rate coefficients for the $C_2H_5O_2NO_2$ dissociation[4] were converted, using modeled equilibrium constants, to recombination rate coefficients at 253 K. A theoretical analysis of the falloff curves using $F_c=0.31$ and $k_\infty=7.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} permitted extrapolation to the low-pressure rate coefficients. The slightly different k_0 value from that of Ref. 1 is due to the use of a different data base and the long and uncertain falloff extrapolation.

(c) Based on the average of the data from Refs. 1 and 2.

Preferred Values

$k_0 = 1.3\times10^{-29}$ $(T/300)^{-6.2}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm0.3$ at 298 K.
$\Delta n = \pm1$.

Comments on Preferred Values

The preferred values are an average of the data from Refs. 1 and 2. The temperature dependence is from the theoretical analysis of Ref. 2. Falloff extrapolations were made with $F_c=0.31$ at 250–300 K such as given from the theoretical analysis of Ref. 2.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
1.0×10^{-11}	254	Elfers, Zabel, and Becker, 1990[1]	(a)
Reviews and Evaluations			
7.5×10^{-12}	200–300	Destriau and Troe, 1990[2]	(b)
8.8×10^{-12}	200–300	IUPAC, 1997[3]	(c)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0. k_∞ was estimated to be similar to the values of k_∞ for the recombination reactions $CCl_3O_2+NO_2$ and $CCl_2FO_2+NO_2$.[3]

(c) See comment (c) for k_0.

Preferred Values

$k=6.1\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_\infty=8.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty=\pm0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

See comments on k_0. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1997.[3]

References

[1] G. Elfers, F. Zabel, and K. H. Becker, Chem. Phys. Lett. **168**, 14 (1990).
[2] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).
[4] F. Zabel, A. Reimer, K. H. Becker, and E. H. Fink, J. Phys. Chem. **93**, 5500 (1989).

$C_2H_5O_2NO_2 + M \rightarrow C_2H_5O_2 + NO_2 + M$

$\Delta H^\circ=67.7$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.8\times10^{-4}\exp(-9285/T)$ [N_2]	245–273	Zabel *et al.*, 1989[1]	FTIR (a)
Reviews and Evaluations			
1.4×10^{-17} [N_2]	298	IUPAC, 1997[2]	(b)
$4.8\times10^{-4}\exp(-9285/T)$ [N_2]	250–300		

Comments

(a) Unimolecular decay of $C_2H_5O_2NO_2$ followed at total pressures ranging from 10 to 800 mbar. Falloff extrapolation with $F_c=0.3$.

(b) Based on theoretical evaluation of Destriau and Troe[3] of the dissociation and recombination data.

Preferred Values

$k_0=1.4\times10^{-17}$ [N_2] s^{-1} at 298 K.

$k_0=4.8\times10^{-4}\exp(-9285/T)$ [N_2] s^{-1} over the temperature range 250–300 K.

Reliability

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

$\Delta(E/R)=\pm1000$ K.

Comments on Preferred Values

The dissociation data are consistent with experimental recombination data (see this evaluation) and the theoretical analysis from Ref. 1. Falloff curves are constructed with $F_c=0.31$ (over the range 250–300 K).

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$8.8\times10^{15}\exp(-10440/T)$	245–273	Zabel *et al.*, 1989[1]	FTIR (a)
Reviews and Evaluations			
$8.8\times10^{15}\exp(-10440/T)$	250–300	IUPAC, 1997[2]	(b)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

Preferred Values

$k=4.0\ \mathrm{s}^{-1}$ at 298 K and 1 bar of air.

$k_\infty-5.4\ \mathrm{s}^{-1}$ at 298 K.

$k_\infty=8.8\times10^{15}\exp(-10440/T)\ \mathrm{s}^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta\log k_\infty=\pm0.5$ at 298 K.

$\Delta(E/R)=\pm1000$ K.

Comments on Preferred Values

See comments on k_0. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1997.[2]

References

[1] F. Zabel, A. Reimer, K. H. Becker, and E. H. Fink, J. Phys. Chem. **93**, 5500 (1989).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

[3] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).

$CH_3C(O)O_2 + NO_2 + M \rightarrow CH_3C(O)O_2NO_2 + M$

$\Delta H^\circ=-119\ \mathrm{kJ\cdot mol^{-1}}$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.1\times10^{-29}\,[N_2]$	298	Basco and Parmar, 1987[1]	FP-AS (a)
$(2.7\pm1.5)\times10^{-28}\,(T/298)^{-7.1}\,[\mathrm{air}]$	248–393	Bridier *et al.*, 1991[2]	FP-AS (b)
Reviews and Evaluations			
$9.7\times10^{-29}\,(T/300)^{-5.6}\,[\mathrm{air}]$	200–300	NASA, 1997[3]	(c)
$2.7\times10^{-28}\,(T/300)^{-7.1}\,[N_2]$	250–300	IUPAC, 1997[4]	(d)

Comments

(a) Photolysis of Cl_2–CH_3CHO–O_2–N_2 and NO_2 at total pressures of 100–800 mbar. Extrapolation of falloff curve with theoretically modeled value of $F_c=0.19$.

(b) The falloff curves were fitted using $F_c=0.30$. The discrepancy with the data of Ref. 1 is attributed to an oversimplified kinetic scheme used in Ref. 1.

(c) Based on the rate data of Bridier *et al.*[2] using $F_c=0.6$.

(d) Based on the rate data of Bridier *et al.*[2] using $F_c=0.3$.

Preferred Values

$k_0 = 2.7\times10^{-28}$ $(T/300)^{-7.1}$ $[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

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

$\Delta n = \pm 2$.

Comments on Preferred Values

The extensive and internally consistent study of $CH_3C(O)OONO_2$ peroxyacetyl nitrate (PAN) formation and dissociation in Ref. 2 is preferred. Falloff extrapolations were performed with a modeled value of $F_c = 0.3$.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
6.1×10^{-12}	298	Basco and Parmar, 1987[1]	FP-AS (a)
$(1.21\pm0.05)\times10^{-11}$ $(T/298)^{-0.9}$	248–393	Bridier *et al.*, 1991[2]	FP-AS (b)
$(1.0\pm0.2)\times10^{-11}$ (0.93 bar)	295	Sehested *et al.*, 1998[5]	PR-A (c)
Reviews and Evaluations			
9.3×10^{-12} $(T/300)^{-1.5}$	200–300	NASA, 1997[3]	(d)
1.2×10^{-11} $(T/300)^{-0.9}$	250–300	IUPAC, 1997[4]	(e)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

(c) $CH_3C(O)O_2$ radicals were generated from the pulse radiolysis of CH_3CHO–O_2–CO_2–NO_2 and CH_3CHO–SF_6–O_2–NO_2 mixtures and the disappearance rate of NO_2 monitored by absorption at 400.5 and 452 nm.

(d) See comment (c) for k_0.

(e) See comment (d) for k_0.

Preferred Values

$k = 1.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_\infty = 1.2\times10^{-11}(T/300)^{-0.9}$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Values

See comments on k_0. The recent measurement of Sehested *et al.*[5] is in excellent agreement with the recommendation. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1997.[4]

References

[1] N. Basco and S. S. Parmar, Int. J. Chem. Kinet. **19**, 115 (1987).
[2] I. Bridier, F. Caralp, H. Loirat, R. Lesclaux, B. Veyret, K. H. Becker, A. Reimer, and F. Zabel, J. Phys. Chem. **95**, 3594 (1991).
[3] NASA Evaluation No. 12, 1997 (see references in Introduction).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).
[5] J. Sehested, L. K. Christensen, T. Møgelberg, O. J. Nielsen, T. J. Wallington, A. Guschin, J. J. Orlando, and G. S. Tyndall, J. Phys. Chem. A **102**, 1779 (1998).

$CH_3C(O)O_2NO_2 + M \rightarrow CH_3C(O)O_2 + NO_2 + M$

$\Delta H° = 119$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.9\pm0.3)\times10^{-3}\exp(-12100/T)\,[N_2]$	300–330	Bridier *et al.*, 1991[1]	FTIR (a)
$1.1\times10^{-20}\,[N_2]$	298*		
Reviews and Evaluations			
4.2×10^{-21} [air]	298	NASA, 1997[2]	(b)
$1.1\times10^{-20}\,[N_2]$	298	IUPAC, 1997[3]	(c)
$4.9\times10^{-3}\exp(-12100/T)\,[N_2]$	300–330		

Comments

(a) Rate of the thermal decomposition of $CH_3C(O)OONO_2$ (PAN) measured by FTIR absorption spectroscopy in the presence of an excess of NO to scavenge CH_3CO_3 radicals. Pressure range 10–790 mbar of N_2. Falloff curves were analyzed with $F_c=0.30$.

(b) Evaluated with the NASA rate coefficients, the equilibrium constant K_c, and $F_c=0.6$.

(c) Based on the data of Ref. 1 using $F_c=0.3$.

Preferred Values

$k_0=1.1\times10^{-20}\,[N_2]\,s^{-1}$ at 298 K.

$k_0=4.9\times10^{-3}\exp(-12100/T)\,[N_2]\,s^{-1}$ over the temperature range 300–330 K.

Reliability

$\Delta \log k_0=\pm0.4$ at 298 K.

$\Delta(E/R)=\pm1000$ K.

Comments on Preferred Values

The data base of Ref. 1 is large enough to allow for a falloff extrapolation to k_0, in part because falloff curves for PAN dissociation and recombination were measured independently. Falloff extrapolations were made with a modeled value of $F_c=0.3$.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.3\pm0.2)\times10^{-4}$	297	Niki *et al.*, 1985[4]	FTIR (a)
2.2×10^{-4}	298	Senum, Fajer, and Gaffney, 1986[5]	FTIR (b)
$2.52\times10^{16}\exp(-13573/T)$	283–313	Tuazon, Carter, and Atkinson, 1991[6]	FTIR (c)
4.2×10^{-4}	298		
$(4.0\pm0.8)\times10^{16}\exp(-13600)/T]$	300–330	Bridier *et al.*, 1991[1]	(d)
6.1×10^{-4}	298*		
$2.5\times10^{17}\exp[-(14340\pm250)/T]$	302–323	Roberts and Bertman, 1992[7]	GC (e)
3.2×10^{-4}	298*		
3.1×10^{-4}	298	Roumelis and Glavas, 1992[8]	GC (f)
$1.6\times10^{16}\exp[-(13539\pm1060)/T]$	288–298	Grosjean, Grosjean, and Williams, 1994[9]	GC (g)
3.0×10^{-4}	298		
Reviews and Evaluations			
4.0×10^{-4}	298	NASA, 1997[2]	(h)
3.8×10^{-4}	298	IUPAC, 1997[3]	(i)
$5.4\times10^{16}\exp(-13830/T)$	300–330		

Comments

(a) Decay of $CH_3CO_3{}^{15}NO_2$ in the presence of $^{14}NO_2$ at a total pressure of 900 mbar of N_2.
(b) Decay of $CH_3CO_3NO_2$ in the presence of NO at a total pressure of 16 mbar.
(c) Thermal decomposition of PAN in an environmental chamber in the presence of 970 mbar of synthetic air or N_2.
(d) See comment (a) for k_0.
(e) Thermal decomposition of PAN at 1 bar total pressure. PAN concentrations were measured by GC with electron capture detection.
(f) Thermal decomposition of PAN in N_2 as well as in the presence of O_2, NO_2, and NO at 1 bar total pressure. The products methyl nitrate and NO_2 in PAN–N_2 mixtures were measured by GC. In the presence of large amounts of O_2, no methyl nitrate was formed at 333 K, indicating that the decomposition of PAN to methyl nitrate and CO_2 does not occur. The data obtained were simulated with 23 reactions.
(g) Thermal decomposition of PAN in 1 bar of air. PAN was measured by GC with electron capture detection.
(h) See comment (b) for k_0.
(i) Based on the rate data reported in Refs. 1 and 6–9.

Preferred Values

$k=3.3\times10^{-4}$ s^{-1} at 298 K and 1 bar of air.
$k_\infty=3.8\times10^{-4}$ s^{-1} at 298 K.
$k_\infty=5.4\times10^{16}\exp(-13830/T)$ s^{-1} over the temperature range 300–330 K.

Reliability

$\Delta\log k_\infty=\pm0.3$ at 298 K.
$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The reported values from Refs. 7–9 are in very good agreement at 298 K but are a factor of two smaller than our 1992 recommendation[10] based on the data of Bridier *et al.*[1] The preferred values attempt to reconcile all measurements. The direct PAN decompositions to methyl nitrate and CO_2[8,11] or to CH_3CO_2 and NO_3 (Ref. 11) are very slow compared to the decomposition to $CH_3CO_3+NO_2$.

References

[1] I. Bridier, F. Caralp, H. Loirat, R. Lesclaux, B. Veyret, K. H. Becker, A. Reimer, and F. Zabel, J. Phys. Chem. **95**, 3594 (1991).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).
[4] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **17**, 525 (1985).
[5] G. I. Senum, R. Fajer, and J. S. Gaffney, J. Phys. Chem. **90**, 152 (1986).
[6] E. C. Tuazon, W. P. L. Carter, and R. Atkinson, J. Phys. Chem. **95**, 2434 (1991).
[7] J. M. Roberts and S. B. Bertman, Int. J. Chem. Kinet. **24**, 297 (1992).
[8] N. Roumelis and S. Glavas, Monatsh. Chem. **123**, 63 (1992).
[9] D. Grosjean, E. Grosjean, and E. L. Williams II, J. Air Waste Manage. Assoc. **44**, 391 (1994).
[10] IUPAC, Supplement IV, 1992 (see references in Introduction).
[11] J. J. Orlando, G. S. Tyndall, and J. G. Calvert, Atmos. Environ. **26A**, 3111 (1992).

$C_2H_5C(O)O_2NO_2+M\rightarrow C_2H_5C(O)O_2+NO_2+M$

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2\times10^{15}\exp(-12800/T)$	300–315	Mineshos and Glavas, 1991[1]	(a)
4.4×10^{-4}	298		
Reviews and Evaluations			
$2\times10^{15}\exp(-12800/T)$	300–315	IUPAC, 1997[2]	(b)

Comments

(a) Thermal decomposition of peroxypropionyl nitrate (PPN) in a 4.5 L glass flask in the presence of 1 bar N_2. PPN and the products ethyl nitrate, NO_2, and methyl nitrate were analyzed by GC at 323 K. In the presence of NO, ethyl nitrate was the major product observed.
(b) See Comments on Preferred Values.

Preferred Values

$k = 4.0 \times 10^{-4}$ s^{-1} at 298 K and 1 bar of air.
$k_\infty = 4.4 \times 10^{-4}$ s^{-1} at 298 K.
$k_\infty = 2 \times 10^{15} \exp(-12800/T)$ s^{-1} over the temperature range 300–315 K.

Reliability
$\Delta \log k_\infty = \pm 0.4$ at 298 K.
$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values

The values from the only reported study of this reaction by Mineshos and Glavas[1] are recommended here.

References

[1] G. Mineshos and S. Glavas, React. Kinet. Catal. Lett. **45**, 305 (1991).
[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3O_2 + NO_3 \rightarrow CH_3O + NO_2 + O_2$ (1)
$\rightarrow$ other products (2)

$\Delta H°(1) = -33.7$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.0 \pm 0.6) \times 10^{-12}$	298	Biggs *et al.*, 1994[1,2]	DF-LIF/AS (a)
$(1.2 \pm 0.6) \times 10^{-12}$	298	Daële *et al.*, 1995[3]	DF-LIF/MS (b)
$(1.3 \pm 0.2) \times 10^{-12}$	298	Helleis, Moortgat, and Crowley, 1996[4]	DF-MS (c)
Branching Ratios			
$k_1/k > 0.9$	298	Kukui, Jungkamp, and Schindler, 1995[5]	DF-LIF/MS (d)
Reviews and Evaluations			
See comment		IUPAC, 1997[6]	(e)

Comments

(a) CH_3O product of reaction (1) measured by LIF; NO_3 by visible absorption spectroscopy. Pressure=3.5 mbar. Modeling of CH_3O time-dependence gave $k/k(CH_3O+NO_3) = 0.43 \pm 0.09$. k calculated with $k(CH_3O+NO_3) = (2.3 \pm 0.7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} obtained in a similar study in the same apparatus.

(b) CH_3O measured by LIF; NO_3 by titration with 2,3-dimethylbutene. The rate coefficient was extracted by numerical simulation from the CH_3O+NO_3 reactant system.

(c) CD_3O_2 decay measured in excess NO_3. k was derived assuming reaction proceeds by channel (1) only; D substitution considered to have negligible influence on k.

(d) Based on observations of DCDO formation from the CD_3O+NO_3 reaction and the relative rates of reactions of CD_3O and CD_3O_2 with NO_3.

(e) In our previous evaluation,[6] no recommendation was made on the basis of the earlier molecular modulation study of Crowley *et al.*[7] which gave a very indirect determination of $k = 2.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Preferred Values

$k = 1.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0$ at 298 K.

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

Comments on Preferred Values

None of the experimental studies for this reaction can be described as definitive. In the flow system method which has been universally used, a quasi-equilibrium between CH_3O_2 and CH_3O radicals is established and concentrations and decay kinetics are influenced by reactions of both radicals. The ratio $k_1/k(CH_3O+NO_3)$ should be well determined but values of 0.43,[1] 0.66,[2] 0.30,[3] and 1.0 (Ref. 4) were obtained. The method used by Helleis *et al.*[4] to determine k_1 is the most direct. Their analysis considers all of the available information on the secondary chemistry and their value[4] is recommended with wide error limits. The value reported by Kukui *et al.*[5] [$k = (3.1 \pm 0.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}] differs substantially from those of Refs. 1–4 and was not included in the evaluation of the rate coefficient. Their work[5] suggests channel (1) is the predominant pathway, with $k_2/k<0.10$.

References

[1] P. Biggs, C. E. Canosa-Mas, J.-M. Fracheboud, D. E. Shallcross, and R. P. Wayne, J. Chem. Soc. Faraday Trans. **90**, 1205 (1994).

[2] P. Biggs, C. E. Canosa-Mas, J.-M. Fracheboud, D. E. Shallcross, and R. P. Wayne, J. Chem. Soc. Faraday Trans. **90**, 1197 (1994).

[3] V. Däele, G. Laverdet, G. Le Bras, and G. Poulet, J. Phys. Chem. **99**, 1470 (1995).

[4] F. Helleis, G. K. Moortgat, and J. N. Crowley, J. Phys. Chem. **100**, 17846 (1996).

[5] A. S. Kukui, T. P. W. Jungkamp, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **99**, 1565 (1995).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

[7] J. N. Crowley, J. P. Burrows, G. K. Moortgat, G. Poulet, and G. Le Bras, Int. J. Chem. Kinet. **25**, 795 (1993).

$C_2H_5O_2+NO_3 \rightarrow C_2H_5O+NO_2+O_2$ (1)

$\rightarrow$ other products (2)

$\Delta H°(1)=-27.3$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.5\pm1.5)\times10^{-12}$	298 K	Biggs *et al.*, 1995[1]	DF-LIF/MS
$(2.3\pm0.5)\times10^{-12}$	298 K	Ray *et al.*, 1996[2]	DF-LIF/MS

Comments

(a) LIF detection of C_2H_5O. Detection of NO_3 by absorption spectroscopy at 662 nm. k was derived by modeling the kinetics of $C_2H_5O_2+NO_3$ in systems using $C_2H_5+O_2$ and $C_2H_5O+NO_3$ to generate $C_2H_5O_2$. Pressure=2.9 mbar of He.

(b) LIF detection of C_2H_5O. MS detection of NO_3. k was derived from a model simulation of system using $C_2H_5O_2$ *as initial reactant, with* NO_3 *in excess.*

Preferred Values

$k=2.3\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

Both studies of this reaction used basically the same technique and gave similar results.[1,2] Extraction of values for k relies on modeling of the reaction system because radical concentrations are controlled by coupling between the $C_2H_5O_2+NO_3$ reaction and the reaction of the product C_2H_5O with NO_3 which regenerates $C_2H_5O_2$. The study of Ray *et al.*[2] gave better defined k values and is the basis of the recommendation. Channel (1) is most important, and Biggs *et al.*[1] suggest that $k_1/k\geqslant0.8$.

References

[1] P. Biggs, C. E. Canosa-Mas, J.-M. Fracheboud, D. E. Shallcross, and R. P. Wayne, J. Chem. Soc. Faraday Trans. **91**, 817 (1995).

[2] A. Ray, V. Daële, I. Vassalli, G. Poulet, and G. LeBras, J. Phys. Chem. **100**, 5737 (1996).

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

$\Delta H^\circ(1) = -333.1\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta H^\circ(2) = 13.6\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta H^\circ(3) = -146.5\ \mathrm{kJ \cdot mol^{-1}}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.2 \pm 0.9) \times 10^{-13}$	298	Cox and Tyndall, 1980[1]	MM-UVAS (a,b)
$(3.7 \pm 0.7) \times 10^{-13}$	298	Sander and Watson, 1980[2]	FP-UVAS (a,c)
$1.40 \times 10^{-13} \exp[(223 \pm 41)/T]$	250–420	Sander and Watson, 1981[3]	FP-UVAS (a,d)
$(3.0 \pm 0.5) \times 10^{-13}$	298		
$(4.4 \pm 1.0) \times 10^{-13}$	298	McAdam, Veyret, and Lesclaux, 1987[4]	FP-UVAS (a,e)
$1.3 \times 10^{-13} \exp[(220 \pm 70/T)]$	228–380	Kurylo and Wallington, 1987[5]	FP-UVAS (a,f)
$(2.7 \pm 0.45) \times 10^{-13}$	298		
$(3.5 \pm 0.5) \times 10^{-13}$	298	Jenkin *et al.*, 1988[6]	MM-UVAS (a,g)
$(3.6 \pm 0.55) \times 10^{-13}$	300	Simon, Schneider, and Moortgat, 1990[7]	MM-UVAS (a,h)
$1.3 \times 10^{-13} \exp(365/T)$	248–573	Lightfoot, Lesclaux, and Veyret, 1990[8]	FP-UVAS (a,i)
$(4.1 \pm 0.9) \times 10^{-13}$	300		
Branching Ratios			
$k_2/k = 1/\{1 + \exp[(1131 \pm 30)/T]/(19 \pm 5)\}$	223–333	Horie, Crowley, and Moortgat, 1990[9]	(j)
$k_2/k = 0.30$	298		
$k_2/k = 0.41 \pm 0.04$	296	Tyndall, Wallington, and Ball, 1998[10]	(k)
$k_3/k < 0.06$	296	Tyndall, Wallington, and Ball, 1998[10]	(k)
Reviews and Evaluations			
$2.5 \times 10^{-13} \exp(190/T)$	200–300	NASA, 1997[11]	(l)
$1.1 \times 10^{-13} \exp(365/T)$	200–400	IUPAC, 1997[12]	(m)

Comments

(a) k is defined by $-d[CH_3O_2/dt = 2k[CH_3O_2]^2$ and was derived from the measured overall second-order decay of CH_3O_2 radicals (k_{obs}) by correcting for secondary removal of CH_3O_2 radicals.

(b) CH_3O_2 by absorption at 250 nm in photolysis of Cl_2–CH_4–O_2 mixtures. $k/\sigma(250\ \mathrm{nm}) = 1.33 \times 10^5$ cm s^{-1}, $\sigma = 3.9 \times 10^{-18}$ cm^2 molecule^{-1} s^{-1} at 250 nm.

(c) Photolysis of $(CH_3)_2N_2 + O_2$ and $Cl_2 + CH_4 + O_2$ mixtures. CH_3O_2 by long path UV absorption. $k/\sigma = (1.06 \pm 0.07) \times 10^5$ cm s^{-1} at 245 nm and $(2.84 \pm 0.36) \times 10^5$ cm s^{-1} at 270 nm. Value quoted is a mean value using σ values obtained by Hochanadel *et al.*[13] Small effects of varying O_2 and adding CO were reported.

(d) Photolysis of $Cl_2 + CH_4 + O_2$ mixtures. σ determined from absorption at $t = 0$ extrapolated from decay curves and estimate of $[CH_3O_2]_0$ from change in Cl_2 concentration in flash. $\sigma(250\ \mathrm{nm}) = (2.5 \pm 0.4) \times 10^{-18}$ cm^2 molecule^{-1} at 298 K. $k/\sigma(250\ \mathrm{nm}) = (5.6 \pm 0.8) \times 10^4 \exp[(223 \pm 41)/T]$ cm s^{-1} (250–420 K).

(e) Photolysis of Cl_2 in the presence of CH_4 and O_2 over the pressure range 169–530 mbar (120–400 Torr). $[CH_3O_2]$ monitored by UV absorption. $k_{obs}/\sigma(250\ \mathrm{nm}) = 1.34 \times 10^5$ cm s^{-1} and $\sigma(250\ \mathrm{nm}) = 4.4 \times 10^{-18}$ cm^2 molecule^{-1}, k_{obs}/k taken to be 1.35.

(f) Photolysis of Cl_2 in the presence of CH_4–O_2–N_2 mixtures at pressures between 67 and 530 mbar (50 and 400 Torr). $k_{obs} = (1.7 \pm 0.4) \times 10^{-13} \exp[(220 \pm 70)/T]$ cm^3 molecule^{-1} s^{-1} determined from measured values of $k_{obs}/\sigma(250)$ by taking $\sigma(250) = 3.30 \times 10^{-18}$ cm^2 molecule^{-1} as previously determined by the same authors. Here we have taken $k_{obs}/k = 1.35$ to calculate k, k_{obs} shown to be independent of pressure (67–530 mbar) at 298 K.

(g) Photolysis of Cl_2 in the presence of CH_4–O_2 mixtures at a total pressure of 1 bar. $k_{obs}/\sigma(250) = 1.11 \times 10^5$ cm s^{-1} and $\sigma(250\ \mathrm{nm}) = (4.25 \pm 0.5) \times 10^{-18}$ cm^2 molecule^{-1} leading to $k_{obs} = (4.7 \pm 0.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Above value of k obtained by taking $k_{obs}/k = 1.35$ to allow for secondary removal of CH_3O_2.

(h) Photolysis of Cl_2 in the presence of CH_4–O_2 mixtures at pressures of 320 mbar (240 Torr). $k_{obs}/\sigma(250\ \text{nm}) = 1.16\times10^5$ cm s^{-1} and $\sigma(250\ \text{nm}) = 4.14\times10^{-18}$ cm^2 molecule^{-1}, leading to $k_{obs} = (4.8\pm0.5)\times10^{-13}$ cm^3 molecule^{-1} s^{-1}. The cited value of k was obtained by taking $k_{obs}/k = 1.35$ to allow for secondary removal of CH_3O_2.

(i) Photolysis of Cl_2 in the presence of $CH_4-O_2-N_2$ mixtures over the pressure range 270–930 mbar (200–700 Torr). CH_3O_2 radicals were monitored by UV absorption, with $k_{obs}/\sigma(210-260\ \text{nm}) = 1.17\times10^5$ cm s^{-1} and $\sigma(250\ \text{mm}) = 4.8\times10^{-18}$ cm^2 molecule^{-1}. k_{obs}/k taken to be 1.35. At temperatures >373 K, the second-order decays of CH_3O_2 were affected by HO_2 radical reactions. The branching ratio was obtained from the effect of HO_2 on the CH_3O_2 decays.

(j) Study of the photooxidation of CH_4, initiated by Cl atoms generated from Cl_2, in a slow-flow system under steady-state illumination. Analysis of HCHO, CH_3OH, and HCOOH products by FTIR spectroscopy.

(k) Photolysis of $CH_3N_2CH_3-O_2$ and $Cl_2-CH_4-O_2$ mixtures, with analyses of reactants and products by FTIR spectroscopy.

(l) k_{298} was based on the data of Cox and Tyndall,[1] Sander and Watson,[3] McAdam *et al.*,[4] Kurylo and Wallington,[5] Jenkin *et al.*,[6] Lightfoot *et al.*,[8] and Simon *et al.*[7] E/R was derived from the data of Sander and Watson,[3] Kurylo and Wallington,[5] Lightfoot *et al.*,[8] and Jenkin and Cox.[14]

(m) See Comments on Preferred Values.

Preferred Values

$k = 3.7\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.1\times10^{-13}\exp(365/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

$k_2 = 1.1\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2 = 5.9\times10^{-13}\exp(-509/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–330 K.

Reliability

$\Delta \log k = \pm0.12$ at 298 K.
$\Delta(E/R) = \pm200$ K.
$\Delta \log k_2 = \pm0.15$ at 298 K.
$\Delta(E_2/R) = \pm300$ K.

Comments on Preferred Values

There have been no new rate coefficient data and our previous recommendation[12] still stands. Here we largely repeat the comments of our last evaluation.

The room temperature measurements of k_{obs}/σ of Refs. 1–8 are in excellent agreement and lead to the recommended value of $k_{obs}/\sigma(250\ \text{nm}) = 1.24\times10^5$ cm s^{-1}. The measurements of the absorption cross section by Simon *et al.*[7] form the basis of our recommendation of $\sigma(250\ \text{nm}) = 3.9\times10^{-18}$ cm^2 molecule^{-1}. Thus, we recommend $k_{obs} = 4.8\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K. Taking the revised branching ratio of $k_2/k = 0.30$ at 298 K, obtained from the expression $k_2/k = 1/\{1+[\exp(1131/T)/19]\}$ yields the slightly revised value of k at 298 K listed above.

The temperature dependence of k reported by Lightfoot *et al.*[8] is in excellent agreement with the studies of Sander and Watson,[3] Kurylo and Wallington,[5] and Jenkin and Cox.[14] Here we have recommended the E/R value of Lightfoot *et al.*[8] on the basis of their more extensive temperature range, and the temperature-dependent branching ratio k_2/k. The recommended Arrhenius equation follows from the recommended values of k_{298} and E/R.

The two studies[8,9] of the temperature dependence of the branching ratio involve different temperature ranges. Here we have selected the results of Horie *et al.*[9] over the more atmospherically relevant temperature range of 200–330 K in calculating the recommended value of k_2. This is derived from the temperature-dependent value of k_2/k[9] and our recommended Arrhenius equation for k.

It should be noted that, from an analysis of their own data[9] together with the results of Lightfoot *et al.*,[8] Anastasi *et al.*,[15] Kan *et al.*,[16] Parkes,[17] Niki *et al.*,[18] and Weaver *et al.*,[19] the equation $k_2/k = 1/\{1+[\exp(1330/T)]/33\}$ was obtained by Horie *et al.*[9] for the more extensive temperature range 223–573 K. This equation shows slight non-Arrhenius behavior. Lightfoot *et al.*[8] observed no pressure dependence of the branching ratio, k_2/k, over the range 0.28–1 bar.

References

[1] R. A. Cox and G. S. Tyndall, J. Chem. Soc. Faraday Trans. 2 **76**, 153 (1980).
[2] S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).
[3] S. P. Sander and R. T. Watson, J. Phys. Chem. **85**, 2960 (1981).
[4] K. McAdam, B. Veyret, and R. Lesclaux, Chem. Phys. Lett. **133**, 39 (1987).
[5] M. J. Kurylo and T. J. Wallington, Chem. Phys. Lett. **138**, 543 (1987).
[6] M. E. Jenkin, R. A. Cox, G. D. Hayman, and L. J. Whyte, J. Chem. Soc. Faraday Trans. 2 **84**, 913 (1988).
[7] F. G. Simon, W. Schneider, and G. K. Moortgat, Int. J. Chem. **22**, 791 (1990).
[8] P. D. Lightfoot, R. Lesclaux, and B. Veyret, J. Phys. Chem. **94**, 700 (1990).
[9] O. Horie, J. N. Crowley, and G. K. Moortgat, J. Phys. Chem. **94**, 8198 (1990).
[10] G. S. Tyndall, T. J. Wallington, and J. C. Ball, J. Phys. Chem. A **102**, 2547 (1998).
[11] NASA Evaluation No. 12, 1997 (see references in Introduction).
[12] IUPAC, Supplement V, 1997 (see references in Introduction).
[13] C. J. Hochanadel, J. A. Ghormley, J. W. Boyle, and P. J. Ogren, J. Phys. Chem. **81**, 3 (1977).
[14] M. E. Jenkin and R. A. Cox, J. Phys. Chem. **95**, 3229 (1991).
[15] C. Anastasi, I. W. M. Smith, and D. A. Parkes, J. Chem. Soc. Faraday Trans. 1 **74**, 1693 (1978).
[16] C. S. Kan, J. G. Calvert, and J. H. Shaw, J. Phys. Chem. **84**, 3411 (1980).
[17] D. A. Parkes, Int. J. Chem. Kinet. **9**, 451 (1977).
[18] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **85**, 877 (1981).
[19] J. Weaver, J. Meagher, R. Shortridge, and J. Heicklen, J. Photochem. **4**, 341 (1975).

$$CH_3O_2 + CH_3C(O)O_2 \rightarrow CH_3O + CH_3CO_2 + O_2 \quad (1)$$

$$\rightarrow CH_3COOH + HCHO + O_2 \quad (2)$$

$\Delta H°(1) = -29$ kJ·mol^{-1}
$\Delta H°(2) = -379$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_1 = (8.8 \pm 1.5) \times 10^{-12}$	298	Roehl, Bauer, and Moortgat, 1996[1]	PLP-UVAS (a)
$k_2 = (1.0 \pm 0.5) \times 10^{-12}$	298		
$8.5 \times 10^{-13} \exp[(726 \pm 25)/T]$	209–358	Maricq and Szente, 1996[2]	PLP-UVAS (b)
$(1.0 \pm 0.2) \times 10^{-11}$	298		
$(8.2 \pm 0.6) \times 10^{-12}$	298	Villenave and Lesclaux, 1996[3]	FP-UVAS (c)
Reviews and Evaluations			
$1.3 \times 10^{-12} \exp(640/T)$	249–367	NASA, 1997[4]	(d)
$5.1 \times 10^{-12} \exp(272/T)$	250–370	IUPAC, 1997[5]	(e)

Comments

(a) Acetyl peroxy radicals were produced from photolysis of Cl_2–CH_3CHO–O_2 mixtures. CH_3O_2 radicals were produced as secondary products, or through added CH_4. k depends on $\sigma(CH_3C(O)O_2)$, for which values of 3.21×10^{-18} cm^2 molecule^{-1} at 240 nm and 6.67×10^{-18} cm^2 molecule^{-1} at 207 nm were obtained, relative to the UV spectrum of $C_2H_5O_2$ [σ(240 nm) $= 4.36 \times 10^{-18}$ cm^2 molecule^{-1}].

(b) As (a) but with UV spectra recorded on gated diode-array spectrometer. $\sigma(CH_3C(O)O_2) = 6.5 \times 10^{-18}$ cm^2 molecule^{-1} at 206 nm and 2.9×10^{-18} cm^2 molecule^{-1} at 250 nm. Channel (2) was concluded to be dominant over the entire 209–358 K temperature range, based on HCHO formation kinetics.

(c) CH_3O_2 radicals were generated simultaneously with $CH_3C(O)O_2$ radicals from the flash photolysis of Cl_2–CH_3CHO–CH_4–O_2 mixtures. For analysis, the branching ratio $\alpha_c (= k_1/k)$ was assumed to be 0.65 but k was found to vary by less than 15% upon varying α_c between 0.5 and 1.0. Overall uncertainty was estimated to be 42% from error propagation analysis.

(d) Based on the work of Moortgat *et al.*[6] and Maricq and Szente.[2]

(e) Based on the work of Moortgat *et al.*[6]

Preferred Values

$k = 9.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.8 \times 10^{-12} \exp(500/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–350 K.

$k_2/k =$ no recommendation.

Reliability

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

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

Comments on Preferred Values

The rate constants measured in the three recent studies,[1–3] which used UV kinetic spectroscopy with similar values of the relevant absorption cross sections, are in good agreement. The preferred value at 298 K is a weighted mean of the values of Roehl *et al.*,[1] Maricq and Szente,[2] and Villenave and Lesclaux.[3] The temperature dependence is a simple average of the values reported by Moortgat *et al.*[6] and Maricq and Szente.[2]

The new recommendation is only slightly lower than our previous IUPAC recommendation[5] which was based on the work of Moortgat *et al.*[6] Lightfoot *et al.*[7] in their review point out that the Moortgat *et al.*[6] value is probably ~20% higher because of the use of cross-sections which were higher than consensus values.

No recommendation is given for the branching ratio. Horie and Moortgat[8] report $k_2/k = 6.1 \times 10^{-6} \exp(2990/T)$ over the temperature range 263–333 K, whereas Maricq and Szente present evidence that k_2 dominates over the entire temperature range 210–350 K. More work is required to resolve this discrepancy.

References

[1] C. M. Roehl, D. Bauer, and C. K. Moortgat, J. Phys. Chem. **100**, 4038 (1996).
[2] M. M. Maricq and J. J. Szente, J. Phys. Chem. **100**, 4507 (1996).
[3] E. Villenave and R. Lesclaux, J. Phys. Chem. **100**, 14372 (1996).
[4] NASA Evaluation No. 12, 1997 (see references in Introduction).
[5] IUPAC, Supplement V, 1997 (see references in Introduction).
[6] G. K. Moortgat, B. Veyret, and R. Lesclaux, J. Phys. Chem. **93**, 2362 (1989).
[7] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).
[8] O. Horie and G. K. Moortgat, J. Chem. Soc. Faraday Trans. **88**, 3305 (1992).

$$CH_3O_2 + CH_3COCH_2O_2 \rightarrow CH_3OH + CH_3COCHO + O_2 \quad (1)$$

$$\rightarrow HCHO + CH_3COCH_2OH + O_2 \quad (2)$$

$$\rightarrow CH_3O + CH_3COCH_2O + O_2 \quad (3)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.8\pm0.4)\times10^{-12}$	298	Bridier *et al.*, 1993[1]	FP-UVA (a)
Branching Ratios			
$k_1/k=0.5\pm0.1$	298	Jenkin *et al.*, 1993[2]	(b)
$k_2/k=0.2\pm0.1$	298		
$k_3/k=0.3\pm0.1$	298	Bridier *et al.*, 1993[1]	(c)
Reviews and Evaluations			
3.8×10^{-12}	298	IUPAC, 1997[3]	(d)

Comments

(a) The total pressure was 1 bar. The overall rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 230 and 260 nm.

(b) Steady-state photolysis of Cl_2 in the presence of CH_3COCH_3–N_2 mixtures at a total pressure of 930 mbar (700 Torr). Branching ratios were deduced from measurements of HCHO and CH_3COCHO products by long-path FTIR spectroscopy and long-path ultraviolet-visible (UV-VIS) diode-array spectroscopy.

(c) Derived from a kinetic analysis of the time-profiles obtained in the experiments described in Comment (a).

(d) Based on the results of Bridier *et al.*[1]

Preferred Values

$k=3.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k=0.5$ at 298 K.
$k_2/k=0.2$ at 298 K.
$k_3/k=0.3$ at 298 K.

Reliability

$\Delta \log k=\pm0.3$ at 298 K.
$\Delta(k_1/k)=\Delta(k_2/k)=\Delta(k_3/k)=\pm0.15$ at 298 K.

Comments on Preferred Values

There have been no new measurements since our previous IUPAC evaluation.[3] The preferred values of the rate coefficient and branching ratios are based on the measurements of Bridier *et al.*[1] and Jenkin *et al.*,[2] and require independent confirmation to reduce the assigned error limits. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[3]

References

[1] I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. 89, 2993 (1993).
[2] M. E. Jenkin, R. A. Cox, M. Emrich, and G. K. Moortgat, J. Chem. Soc. Faraday Trans. 89, 2983 (1993).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$HOCH_2O_2 + HOCH_2O_2 \rightarrow HCOOH + CH_2(OH)_2 + O_2$ (1)

$\rightarrow 2HOCH_2O + O_2$ (2)

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_1 = 5.65 \times 10^{-14} \exp[(750 \pm 400)/T]$	275–323	Veyret *et al.*, 1989[1]	(a,b)
$k_1 = (7.0 \pm 2.1) \times 10^{-13}$	295		
$k_1 = (5.6 \pm 2.8) \times 10^{-13}$	298	Burrows *et al.*, 1989[2]	(a,c)
Relative Rate Coefficients			
$k_2 = (5.5 \pm 1.1) \times 10^{-12}$	298	Burrows *et al.*, 1989[2]	(a,c)
Reviews and Evaluations			
$k_1 = 5.7 \times 10^{-14} \exp(750/T)$	275–325	IUPAC, 1997[3]	(d)
$k_2 = 5.5 \times 10^{-12}$	298		

Comments

(a) k is defined by $-d[HOCH_2O_2]dt = 2k[HOCH_2O_2]$.[2]

(b) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2, with time-resolved absorption spectroscopy for the detection of HO_2 and $HOCH_2O_2$ radicals. The rate coefficient k_1 was obtained from a computer fit of the absorption profiles of $HOCH_2O_2$ radicals at 250 nm. Channel (2) leads to the regeneration of HO_2 radicals and was thus not observable in this system.

(c) Molecular modulation study of Cl_2–HCHO–O_2 mixtures with diode laser infrared spectroscopy for the detection of HO_2 radicals and UV spectroscopy for $HOCH_2O_2$ radicals. The rate coefficient k_2 was obtained from a computer simulation of quantum yields for HCOOH formation.

(d) See Comments on Preferred Values.

Preferred Values

$k_1 = 7.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 5.7 \times 10^{-14} \exp(750/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–330 K.

$k_2 = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.

$\Delta(E_1/R) = \pm 750$ K.

$\Delta \log k_2 = \pm 0.3$ at 298 K.

Comments on Preferred Values

The parallel studies of Veyret *et al.*[1] and Burrows *et al.*[2] confirm that the interaction of $HOCH_2O_2$ radicals involves two channels. The two reports[1,2] of the rate coefficient k_1 at room temperature are in good agreement, and indicate that this channel is a factor of ~3–4 faster than the analogous interaction of CH_3O_2 radicals. The rate coefficient k_2 is even higher than k_1, with a value ~50 times that of the analogous reaction of CH_3O_2 radicals. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[3] Confirmation of the temperature coefficient of k_1 is needed, as well as a determination of the temperature coefficient of k_2.

References

[1] B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K. Moortgat, J. Phys. Chem. **93**, 2368 (1989).

[2] J. P. Burrows, G. K. Moortgat, G. S. Tyndall, R. A. Cox, M. E. Jenkin, G. D. Hayman, and B. Veyret, J. Phys. Chem. **93**, 2375 (1989).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$$C_2H_5O_2 + C_2H_5O_2 \rightarrow C_2H_5OH + CH_3CHO + O_2 \quad (1)$$

$$\rightarrow 2C_2H_5O + O_2 \quad (2)$$

$$\rightarrow C_2H_5OOC_2H_5 + O_2 \quad (3)$$

$\Delta H^\circ(1) = -343.2\ \mathrm{kJ \cdot mol^{-1}}$

$\Delta H^\circ(2) = 26.4\ \mathrm{kJ \cdot mol^{-1}}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.0 \pm 0.1) \times 10^{-13}$	298	Adachi, Basco, and James, 1979[1]	FP-UVA (a,b)
$2.7 \times 10^{-13} \exp(-470/T)$	302–373	Anastasi, Waddington, and Woolley, 1983[2]	MM-UVA (a,c)
5.6×10^{-14}	298		
8.1×10^{-14}	266–348	Cattell *et al.*, 1986[3]	MM-UVA (a,d)
$8.5 \times 10^{-14} \exp[-(110 \pm 40)/T]$	228–380	Wallington, Dagaut, and Kurylo, 1988[4]	FP-UVA (a,e)
5.9×10^{-14}	298		
$6.7 \times 10^{-14} \exp[(60 \pm 40)/T]$	248–460	Fenter *et al.*, 1993[5]	FP-UVA (a,f)
$(7.9 \pm 0.5) \times 10^{-14}$	298		
6.7×10^{-14}	298	Bauer, Crowley, and Moortgat, 1992[6]	MM-UVA (a,g)
$(7.3 \pm 2.4) \times 10^{-14}$	295	Atkinson and Hudgens, 1997[7]	PLP-UVA (a,h)
Branching Ratios			
$k_1/k_2 = 0.76$	298	Niki *et al.*, 1982[8]	(i)
$k_1/k_2 = 0.60$	298	Anastasi, Waddington, and Woolley, 1983[2]	(c)
$k_1/k_2 = 0.49$	298	Wallington *et al.*, 1989[9]	(j)
Reviews and Evaluations			
6.8×10^{-14}	200–300	NASA, 1997[10]	(k)
6.4×10^{-14}	250–450	IUPAC, 1997[11]	(l)

Comments

(a) k is defined by $-d[C_2H_5O_2]/dt = 2k[C_2H_5O_2]^2$ and obtained from the overall decay constant k_{obs} corrected for secondary removal of $C_2H_5O_2$ radicals.

(b) k determined by simulation of $C_2H_5O_2$ radical decay using complex mechanism accounting for secondary removal of $C_2H_5O_2$ radicals.

(c) Photolysis of $(C_2H_5)_2N_2$ in the presence of O_2 (7–200 mbar) and N_2 (550–730 mbar). $k/\sigma(240\ \mathrm{nm})$ and $\sigma(240\ \mathrm{nm})$ found to be temperature dependent. Branching ratios determined from analysis of products C_2H_5OH and CH_3CHO by GC. The data cited are derived from the rate coefficients k_1 and k_2 given in Table 6 of Anastasi *et al.*[2]

(d) Photolysis of Cl_2–C_2H_6–O_2–N_2 mixtures. Pressure =3–1000 mbar. $k_{obs}/\sigma(260\ \mathrm{nm}) = (4.07 \pm 0.04) \times 10^4$ cm s^{-1} and $\sigma(260\ \mathrm{nm}) = (3.20 \pm 0.38) \times 10^{-18}$ cm^2 molecule^{-1} leading to $k_{obs} = (1.30 \pm 0.16) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Cited value of k obtained by taking $k_{obs}/k = 1.6$.

(e) $k_{obs} = (1.41 \pm 0.19) \times 10^{-13} \exp[-(110 \pm 40)/T]$ cm^3 molecule^{-1} s^{-1} based on temperature independent value of $\sigma(250\ \mathrm{nm}) = (3.89 \pm 0.54) \times 10^{-18}$ cm^2 molecule^{-1} and $k_{obs}/k = 1.66$.

(f) Flash photolysis–UV absorption study of Cl_2–C_2H_6–O_2–N_2 mixtures at 1 bar total pressure. Rate coefficients were derived from simultaneous computer analyses of several decay curves collected at different wavelengths. The value of $k_{obs} = (1.40 \pm 0.11) \times 10^{-13} \exp[-(20 \pm 40)/T]$ cm^3 molecule^{-1} s^{-1} was corrected at each temperature by dividing by $(1+\alpha)$, where $\alpha = \beta/(1+\beta)$ and $\beta = 10.2 \exp(-533/T)$.

(g) Molecular modulation study. $C_2H_5O_2$ radicals were generated from the photolysis of flowing mixtures of Cl_2–C_2H_6–O_2–N_2 at a total pressure of 133 mbar (100 Torr) and monitored by absorption at 210 and 330 nm. Values of k/σ were determined at 220, 250, and 280 nm, leading to $k_{obs} = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The cited value of k was calculated taking $k_2/k = 0.65$.

(h) Photolysis of Cl_2–C_2H_6–O_2–Ar mixtures at (7.3 ± 1.0) mbar total pressure with $C_2H_5O_2$ radicals being monitored by UV cavity ring-down spectroscopy at 265 and 270 nm. The measured value of k_{obs} was corrected for secondary reactions by taking $k_{obs}/k = 1.7$.

(i) Products CH_3CHO, C_2H_5OH, and C_2H_5OOH monitored by FTIR.

(j) Photolysis of Cl_2–C_2H_6 mixtures in 930 mbar (700 Torr) air. Products monitored by FTIR.

(k) k_{298} was calculated from the mean k_{obs} value from the studies of Cattell *et al.*,[3] Wallington *et al.*,[4] Bauer *et al.*,[6] and Fenter *et al.*,[5] and corrected for secondary removal of $C_2H_5O_2$ radicals by the use of $k_2/k=0.6$. E/R was from the studies of Anastasi *et al.*,[2] Cattell *et al.*,[3] Wallington *et al.*,[4] Bauer *et al.*,[6] and Fenter *et al.*[5]

(l) See Comments on Preferred Values.

Preferred Values

$k=6.4\times10^{-14}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–450 K.

$k_2/k=0.62$ at 298 K.

Reliability

$\Delta \log k=\pm0.12$ at 298 K.

$\Delta(E/R)=^{+300}_{-100}$ K.

$\Delta(k_2/k)=\pm0.1$ at 298 K.

Comments on Preferred Values

The rate coefficients for this reaction have all been determined using UV absorption to monitor $C_2H_5O_2$, and hence the measured quantity is k/σ where σ is the absorption cross-section at the monitoring wavelength. The data for k_{298} are generally in good agreement. The most recent temperature coefficient reported by Fenter *et al.*[5] ($E/R=-60$ K) agrees with the earlier data of Cattell *et al.*[3] ($E/R\simeq0$ K) but less well with those of Anastasi *et al.*[2] ($E/R=470$ K), Wallington *et al.*[8] ($E/R=110$ K) or Bauer *et al.*[6] ($E/R=-230$ K). In view of the small temperature coefficients reported in most of these studies, together with the relatively large associated error limits, we have selected a temperature-independent rate coefficient k based on k_{298}. Thus, from the data of Adachi *et al.*,[1] Anastasi *et al.*,[2] Cattell *et al.*,[3] Wallington *et al.*,[4] Bauer *et al.*,[6] and Fenter *et al.*,[5] the average value of $k_{obs}=1.03\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K. Taking $k_2/k=0.62$ at 298 K (the mean of the data of Niki *et al.*,[8] Anastasi *et al.*,[2] and Wallington *et al.*[9]) yields the recommended value of $k_{298}=6.4\times10^{-14}$ cm^3 molecule^{-1} s^{-1}. The data of Wallington *et al.*[9] show that $k_3/k\leq0.06$. The rate coefficient of Atkinson and Hudgens[7] is in agreement with the recommendation.

The temperature dependence of the branching ratio reported by Anastasi *et al.*[2] still requires confirmation.

References

[1] H. Adachi, N. Basco, and D. G. L. James, Int. J. Chem. Kinet. **11**, 1211 (1979).

[2] C. Anastasi, D. J. Waddington, and A. Woolley, J. Chem. Soc. Faraday Trans. 1 **79**, 505 (1983).

[3] F. C. Cattell, J. Cavanagh, R. A. Cox, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. 2 **82**, 1999 (1986).

[4] T. J. Wallington, P. Dagaut, and M. J. Kurylo, J. Photochem. **42**, 173 (1988).

[5] F. F. Fenter, V. Catoire, R. Lesclaux, and P. D. Lightfoot, J. Phys. Chem. **97**, 3530 (1993).

[6] D. Bauer, J. N. Crowley, and G. K. Moortgat, J. Photochem. Photobiol. **A65**, 329 (1992).

[7] D. B. Atkinson and J. W. Hudgens, J. Phys. Chem. A **101**, 3901 (1997).

[8] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **86**, 3825 (1982).

[9] T. J. Wallington, C. A. Gierczak, J. C. Ball, and S. M. Japar, Int. J. Chem. Kinet. **21**, 1077 (1989).

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

[11] IUPAC, Supplement V, 1997 (see references in Introduction).

$$C_2H_5O_2 + CH_3C(O)O_2 \rightarrow C_2H_5O + CH_3CO_2 + O_2 \quad (1)$$

$$\rightarrow CH_3CHO + CH_3C(O)OH + O_2 \quad (2)$$

$\Delta H°(1)=-22.0$ kJ·mol^{-1}

$\Delta H°(2)=-397.1$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.0\pm0.3)\times10^{-11}$	298	Villenave and Lesclaux, 1996[1]	FP-UVAS

Comments

(a) Flash photolysis of Cl_2–C_2H_6–CH_3CHO–O_2 mixtures. $CH_3C(O)O_2$ and $C_2H_5O_2$ radical concentrations were determined by fitting absorption-time data at 207 and 240 nm, using cross-sections recommended in Lightfoot *et al.*[2] Complex reaction mechanism with $\alpha_c(=k_1/k)$ assumed to be 0.82. The overall uncertainty was estimated as 54%.

Preferred Values

$k=1.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is based on the only reported experimental study made using a well-established technique. The recommended uncertainty reflects the need to account for complex secondary chemistry in deriving the rate coefficient and deconvolution of overlapping UV spectra.

References

[1] E. Villenave and R. Lesclaux, J. Phys. Chem. **100**, 14372 (1996).
[2] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).

$CH_3OCH_2O_2 + CH_3OCH_2O_2 \rightarrow CH_3OCH_2OH + CH_3OCHO + O_2$ (1)

$\rightarrow 2CH_3OCH_2O + O_2$ (2)

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.3) \times 10^{-12}$	298	Jenkin *et al.*, 1993[1]	(a,b)
Branching Ratios			
$k_2/k = 0.67 \pm 0.11$	295	Jenkin *et al.*, 1993[1]	(c)
$k_2/k = 0.67 \pm 0.13$	298	Jenkin *et al.*, 1993[1]	(d)
Reviews and Evaluations			
2.1×10^{-12}	298	IUPAC, 1997[2]	(f)

Comments

(a) k is defined by $-d[CH_3OCH_2O_2]/dt = 2k[CH_3OCH_2O_2]^2$ and has been derived from the measured overall second-order decay of $CH_3OCH_2O_2$ radicals (k_{obs}).

(b) Molecular modulation study of Cl_2–CH_3OCH_3–O_2–N_2 mixtures together with a pulse radiolysis study of SF_6–CH_3OCH_3–O_2 mixtures. k_{obs} was found to be dependent on the total pressure (23–1013 mbar) and on the composition of the reaction mixture. On the basis of a mechanism involving the generation of H atoms via the reaction $CH_3OCH_2O + M \rightarrow CH_3OCHO + H + M$, it was possible to derive the above pressure-independent value of k.

(c) FTIR spectroscopic study of the steady-state photolysis of Cl_2 in the presence of CH_3OCH_3–O_2–N_2 mixtures over the total pressure range 13–930 mbar (10–700 Torr). The branching ratio was determined from the yields of CH_3OCHO and CH_3OCH_2OOH. Minor amounts of CH_3OCH_2OH were also observed.

(d) Similar study to that described in comment (c). The branching ratio and k were derived from a kinetic analysis of the effects of $[O_2]$ and $[Cl_2]$ on k_{obs}, based on a mechanism including the production of H atoms from the reaction $CH_3OCH_2O + M \rightarrow CH_3OCHO + H + M$.

(e) See Comments on Preferred Values.

Preferred Values

$k = 2.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.67$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The apparent effect of total pressure on k, the first reported for this type of reaction,[3] has been shown to be an artifact by the more recent experiments of Jenkin *et al.*[1] This comprehensive study, on which the recommendation is based, has shown that the pressure effect was due to secondary chemistry involving H atoms which arise from the reaction $CH_3OCH_2O + M \rightarrow CH_3OCHO + H + M$. A kinetic analysis of the molecular modulation system, allowing for secondary chemistry, yielded the preferred rate coefficient. At the same time the derived value of the branching ratio, k_2/k, is in excellent agreement with that obtained from a steady-state photolysis system with FTIR spectroscopic analyses.[1] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[2]

References

[1] M. E. Jenkin, G. D. Hayman, T. J. Wallington, M. D. Hurley, J. C. Ball, O. J. Nielsen, and T. Ellermann, J. Phys. Chem. **97**, 11712 (1993).
[2] IUPAC, Supplement V, 1997 (see references in Introduction).
[3] P. Dagaut, T. J. Wallington, and M. J. Kurylo, J. Photochem. Photobiol. **48**, 187 (1989).

$CH_3C(O)O_2 + CH_3C(O)O_2 \rightarrow 2CH_3C(O)O + O_2$

$\Delta H° = -71$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.8×10^{-12} exp[(530±100)/T]	253–368	Moortgat, Veyret, and Lesclaux, 1989[1]	FP-UVAS (a)
$(1.6 \pm 0.3) \times 10^{-11}$	298		
$(1.36 \pm 0.19) \times 10^{-11}$	298	Roehl, Bauer, and Moortgat, 1996[2]	PLP-UVAS (b)
3.0×10^{-12} exp[(504±114)/T]	209–358	Maricq and Szente, 1996[3]	PLP-UVAS (c)
1.5×10^{-11}	298		
Reviews and Evaluations			
2.9×10^{-12} exp(500/T)	250–360	NASA, 1997[4]	(d)
2.8×10^{-12} exp(530/T)	250–370	IUPAC, 1997[5]	(e)

Comments

(a) k determined using absorption cross-sections for $CH_3C(O)O_2$ and CH_3O_2 radicals approximately 20% higher than later consensus. $CH_3C(O)O_2$ radicals were produced by photolysis of Cl_2–CH_3CHO–O_2 mixtures.

(b) k determined using absorption cross-sections of $\sigma = 6.67 \times 10^{-18}$ cm^2 molecule^{-1} at 207 nm for $CH_3C(O)O_2$. Source of $CH_3C(O)O_2$ radicals as in (a). Detailed analysis of secondary chemistry.

(c) Based on $\sigma(CH_3C(O)O_2) = 6.5 \times 10^{-18}$ cm^2 molecule^{-1} at 206 nm. Source of $CH_3C(O)O_2$ radicals as in (a). Detailed analysis of secondary chemistry.

(d) Based on the data of Moortgat *et al.*,[1] Roehl *et al.*,[2] and Maricq and Szente.[3]

(e) Based on the data of Moortgat *et al.*[1]

Preferred Values

$k = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.9 \times 10^{-12}$ exp(500/T) cm^3 molecule^{-1} s^{-1} over the temperature range 200–370 K.

Reliability

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

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

Comments on Preferred Values

All three studies,[1–3] taking proper account of the complex secondary chemistry following recombination of $CH_3C(O)O_2$ radicals and of the magnitude and overlap of the UV absorptions due to acetylperoxy, methylperoxy, and hydroperoxy radicals, now give results in good agreement for k and its temperature dependence. The recommendation is thus based on the data of Moortgat *et al.*,[1] Roehl *et al.*,[2] and Maricq and Szente.[3]

References

[1] G. K. Moortgat, B. Veyret, and R. Lesclaux, J. Phys. Chem. **93**, 2362 (1989).

[2] C. M. Roehl, D. Bauer, and G. K. Moortgat, J. Phys. Chem. **100**, 4038 (1996).

[3] M. M. Maricq and J. J. Szente, J. Phys. Chem. **100**, 4507 (1996).

[4] NASA Evaluation No. 12, 1997 (see references in Introduction).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

$$CH_3CO_3 + CH_3COCH_2O_2 \rightarrow CH_3COOH + CH_3COCHO + O_2 \quad (1)$$

$$\rightarrow CH_3CO_2 + CH_3COCH_2O + O_2 \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.0 \pm 2.0) \times 10^{-12}$	298	Bridier *et al.*, 1993[1]	(a)
$k_1 \leq 4 \times 10^{-12}$	298		
Branching Ratios			
$k_2/k = 0.5 \pm 0.2$	298	Jenkin *et al.*, 1993[2]	(b)
Reviews and Evaluations			
5.0×10^{-12}	298	IUPAC, 1997[3]	(c)

Comments

(a) Flash photolysis of Cl_2 in the presence of CH_3COCH_3–CH_3CHO–N_2 mixtures at a total pressure of 1 bar (760 Torr). The rate coefficient k was derived from a kinetic analysis of absorption–time profiles measured at 210, 220, 230, and 245 nm, using the value of $k_2/k = 0.5$ determined by Jenkin *et al.*[2]

(b) Steady state photolysis of Cl_2 in the presence of CH_3COCH_3–N_2 mixtures at a total pressure of 930 mbar (700 Torr). The branching ratio was deduced from measurements of HCHO and CH_3COCHO products by long-path FTIR spectroscopy and long-path UV/visible diode-array spectroscopy.

(c) See Comments on Preferred Values.

Preferred Values

$k = 5.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.5$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(k_2/k) = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred values of the rate coefficient and the branching ratio are from the studies of Bridier *et al.*[1] and Jenkin *et al.*,[2] and require independent confirmation. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[3]

References

[1] I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. **89**, 2993 (1993).
[2] M. E. Jenkin, R. A. Cox, M. Emrich, and G. K. Moortgat, J. Chem. Soc. Faraday Trans. **89**, 2983 (1993).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$$HOCH_2CH_2O_2 + HOCH_2CH_2O_2 \rightarrow HOCH_2CH_2OH + HOCH_2CHO + O_2 \quad (1)$$

$$\rightarrow 2HOCH_2CH_2O + O_2 \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.3) \times 10^{-12}$	296	Murrells *et al.*, 1991[1]	PLP/MM-UVAS (a)
$(2.1 \pm 0.3) \times 10^{-12}$	298	Jenkin and Hayman, 1995[2]	MM-UVAS (b)
$7.8 \times 10^{-14} \exp[(1000 \pm 80)/T]$	300–470	Boyd and Lesclaux, 1997[3]	PLP-UVAS
$(2.2 \pm 0.3) \times 10^{-12}$	298		(c)
Branching Ratios			
$k_2/k = 0.5 \pm 0.1$	298	Barnes, Becker, and Ruppert, 1993[4]	P (d)
$k_2/k = 0.55$	298	Boyd and Lesclaux, 1997[3]	PLP-UVAS (e)
Reviews and Evaluations			
2.3×10^{-12}	298	IUPAC, 1997[5]	(f)

Comments

(a) Separate pulsed laser photolysis and molecular modulation studies using the photolysis of H_2O_2 to produce OH radicals in the presence of ethene and air. Pressure = 1 bar N_2. $HOCH_2CH_2O_2$ radicals were monitored by UV absorption at 250 nm with $\sigma_{250} = 4.7 \times 10^{-18}$ cm^2 molecule^{-1} (mean value). $k_{obs}/\sigma_{250} = 6.7 \times 10^5$ cm s^{-1}. k was calculated from the laser photolysis experiments with $k_2/k = 0.36$.

(b) Identical technique to that in note (a). $k_{obs}/\sigma_{250} = (7.1 \pm 0.6) \times 10^5$ cm s^{-1}. k calculated using $k_2/k = 0.5$ and using data from Ref. 1 in addition.

(c) Pulsed laser photolysis of H_2O_2 at 248 nm in the presence of ethene and O_2. $HOCH_2CH_2O_2$ radicals were monitored by absorption at 250 nm.

(d) Analysis of products by FTIR in the photolysis of $HOCH_2CH_2I$ or H_2O_2–C_2H_4 mixtures in $O_2 + N_2$. Pressure 150–900 mbar. Mean value given from both systems, which were in excellent agreement, and independent of total pressure or O_2 concentration.

(e) Based on HO_2 radical formation from the $HOCH_2CH_2O + O_2$ reaction, measured by UV absorption at 220 nm.

(f) Based on the data of Murrells *et al.*[1] and the branching ratio of Barnes *et al.*[4]

Preferred Values

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

$k = 7.8 \times 10^{-14} \exp(1000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–450 K.

$k_2 = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 300$ K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

All the recent studies of this reaction provide consistent and seemingly reliable values for the rate coefficient and for the branching ratio.[1–4] The preferred value at 298 K is a mean of the values reported by Murrells *et al.*,[1] Jenkin and Hayman,[2] and Boyd and Lesclaux,[3] and the branching ratio accepts the value of Barnes *et al.*[4] The temperature dependence from the work of Boyd and Lesclaux[3] is recommended but with wider error limits on E/R. A measurement of the temperature dependence of the branching ratio would be of interest.

References

[1] T. P. Murrells, M. E. Jenkin, S. J. Shalliker, and G. D. Hayman, J. Chem. Soc. Faraday Trans. **87**, 2351 (1991).

[2] M. E. Jenkin and G. D. Hayman, J. Chem. Soc. Faraday Trans. **91**, 1911 (1995).

[3] A. A. Boyd and R. Lesclaux, Int. J. Chem. Kinet. **39**, 323 (1997).

[4] I. Barnes, K. H. Becker, and L. Ruppert, Chem. Phys. Lett. **203**, 295 (1993).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

$$n\text{-}C_3H_7O_2 + n\text{-}C_3H_7O_2 \rightarrow n\text{-}C_3H_7OH + C_2H_5CHO + O_2 \quad (1)$$

$$\rightarrow 2n\text{-}C_3H_7O + O_2 \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.3 \pm 0.3) \times 10^{-13}$	298	Adachi and Basco, 1982[1]	FP-UVA (a), (b)
Reviews and Evaluations			
$k = 3.0 \times 10^{-13}$	298	IUPAC, 1997[2]	(c)

Comments

(a) k is defined by $-d[n\text{-}C_3H_7O_2] = 2k[n\text{-}C_3H_7O_2]^2$ and has been derived from the measured overall second order decay of $n\text{-}C_3H_7O_2$ radicals (k_{obs}) by correcting for secondary removal of $n\text{-}C_3H_7O_2$ radicals.

(b) Monitoring wavelength for $n\text{-}C_3H_7O_2$ radicals was 260 nm, with $\sigma = 3.15 \times 10^{-18}$ cm^2 molecule^{-1}. The rate coefficient derived from $k_{obs} = (3.84 \pm 0.33) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} on the basis of a mechanism with 12 secondary reactions.

(c) See Comments on Preferred Values.

Preferred Values

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

Reliability

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

Comments on Preferred Values

The recommended rate coefficient is the rounded-off value from the study of Adachi and Basco,[1] and is identical to that in our previous evaluation, IUPAC, 1997.[2] The room-temperature rate coefficient requires substantiation along with a determination of the temperature coefficient.

The recommended value of k_{298} is in line with the rate coefficients of the analogous reactions of the CH_3O_2 and $C_2H_5O_2$ radicals. On the other hand, the recommended rate coefficient for the self-reaction of the $i\text{-}C_3H_7O_2$ radical is considerably lower ($k_{298} = 1.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}) and that reported[3] for the $t\text{-}C_4H_9O_2$ radical is even lower still ($k_{298} = 2.3 \times 10^{-17}$ cm^3 molecule^{-1} s^1). This trend is in keeping with that observed in the liquid phase for the RO_2 radical interactions,[4] i.e., k(primary RO_2) $>$ k(secondary RO_2) $>$ k(tertiary RO_2).

References

[1] H. Adachi and N. Basco, Int. J. Chem. Kinet. **14**, 1125 (1982).
[2] IUPAC, Supplement V, 1997 (see references in Introduction).
[3] C. Anastasi, I. W. M. Smith, and D. A. Parkes, J. Chem. Soc. Faraday Trans. 1 **74**, 1693 (1978).
[4] J. E. Bennett, D. M. Brown, and B. Mile, Trans. Faraday Soc. **66**, 386 (1970).

$$i\text{-}C_3H_7O_2 + i\text{-}C_3H_7O_2 \rightarrow i\text{-}C_3H_7OH + CH_3COCH_3 + O_2 \quad (1)$$

$$\rightarrow 2\,i\text{-}C_3H_7O + O_2 \quad (2)$$

$\Delta H°(1) = -351.9$ kJ·mol^{-1}
$\Delta H°(2) = 33.2$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.43\times10^{-12}\exp[-(2243\pm69)/T]$	300–373	Kirsch *et al.*, 1978[1]	(a,b)
8.10×10^{-16}	300		
$(1.3\pm0.4)\times10^{-15}$	298	Adachi and Basco, 1989[2]	(a,c)
$(5.3\pm0.5)\times10^{-14}$	298	Munk *et al.*, 1986[3]	(a,d)
Branching Ratios			
$k_2/k_1 = 1.39\pm0.04$	302	Kirsch *et al.*, 1979[4]	(e)
$k_2/k_1 = 56.3\exp(-1130/T)$	302–372	Cowley, Waddington, and Woolley, 1982[5]	(f)
Reviews and Evaluations			
$1.6\times10^{-12}\exp(-2200/T)$	300–400	IUPAC, 1997[6]	(g)

Comments

(a) k is defined by $-d[i\text{-}C_3H_7O_2]/dt = 2k[i\text{-}C_3H_7O_2]^2$ and has been derived from the measured overall second-order decay of $i\text{-}C_3H_7O_2$ radicals (k_{obs}) by correcting for secondary removal of $i\text{-}C_3H_7O_2$ radicals.

(b) Molecular modulation study of the photolysis of 2,2′-azopropane in the presence of O_2 and N_2 at total pressures up to 950 mbar (710 Torr). $i\text{-}C_3H_7O_2$ radicals were monitored by absorption at 265 nm. The rate coefficient k has been calculated from the experimental value of $k_{obs} = (2.37\pm0.17)\times10^{-12}\exp[-(2243\pm60)/T]$ cm^3 molecule^{-1} s^{-1} and the branching ratio $k_2/k_1 = 1.39$ at 302 K determined in the subsequent study.[4]

(c) Flash photolysis of 2,2′-azopropane in the presence of O_2 and added N_2 at total pressures up to 960 mbar (720 Torr). $i\text{-}C_3H_7O_2$ radicals were monitored by absorption at 240 nm, for which $\sigma(240\text{ nm}) = 4.86\times10^{-18}$ cm^2 molecule^{-1}. The rate coefficient k has been calculated from the experimental value of $k_{obs} = (2.03\pm0.58)\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K, on the basis of a proposed mechanism of 12 elementary reactions including secondary consumption of $i\text{-}C_3H_7O_2$ radicals.

(d) Pulse radiolysis of H_2 at 1 bar in the presence of C_3H_6, $i\text{-}C_3H_7$ radicals were generated from the reaction of H atoms with C_3H_6. The absorption spectrum of the $i\text{-}C_3H_7O_2$ radical was observed on the addition of O_2 and the decay of $i\text{-}C_3H_7O_2$ radicals monitored by UV absorption at 253 nm, and found to obey second-order kinetics. It is not clear if the reported value of the rate coefficient is k_{obs} or k.

(e) Steady-state photolysis of 2,2′-azopropane in the presence of O_2 and added N_2 at total pressures up to 670 mbar (500 Torr). Ratio of rate coefficients based on analyses of CH_3COCH_3 and $(CH_3)_2CHOH$ by GC.

(f) Extension of the experiments by Kirsch *et al.*,[4] to obtain k_2/k_1 at 333 and 372 K. The Arrhenius equation calculated from these data and a value of k_2/k_1 at 302 K was reported by Kirsch *et al.*[4]

(g) See Comments on Preferred Values.

Preferred Values

$k = 1.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.6\times10^{-12}\exp(-2200/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–400 K.

$k_1/k = 0.44$ at 298 K.

$k_1/k = 3.7\times10^{-2}\exp(740/T)$ over the temperature range 300–400 K.

$k_2/k = 0.56$ at 298 K.

$k_2/k = 2.0\exp(-380/T)$ over the temperature range 300–400 K.

Reliability

$\Delta\log k = \pm0.3$ at 298 K.
$\Delta(E/R) = \pm300$ K.
$\Delta(k_1/k) = \Delta(k_2/k) = \pm0.15$ at 298 K.

Comments on Preferred Values

The recommended rate coefficient (k) at 298 K is the average of the rate coefficients from the data of Kirsch *et al.*[1] and Adachi and Basco,[2] which are in reasonable agreement. We have not taken into account the rate coefficient reported by Munk *et al.*,[3] for which experimental details are lacking. The recommended temperature dependence of k is based on the results of Kirsch *et al.*,[1] which have been rounded off and adjusted to the recommended value of k_{298}.

The measurements of the branching ratio and its temperature dependence[4,5] appear to be reliable and have been adopted here, but require further confirmation. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[6]

The value of k_{298} is considerably lower than that for the analogous reaction of the n-$C_3H_7O_2$ radical, which is in keeping with the trend observed in studies of the interactions of alkylperoxy radicals in solution,[7] i.e., $k(\text{primary } RO_2) > k(\text{secondary } RO_2) > k(\text{tertiary } RO_2)$.

References

[1] L. J. Kirsch, D. A. Parkes, D. J. Waddington, and A. Woolley, J. Chem. Soc. Faraday Trans. 1 **74**, 2293 (1978).

[2] H. Adachi and N. Basco, Int. J. Chem. Kinet. **14**, 1125 (1982).

[3] J. Munk, P. Pagsberg, E. Ratajczak, and A. Sillesen, Chem. Phys. Lett. **132**, 417 (1986).

[4] L. J. Kirsch, D. A. Parkes, D. J. Waddington, and A. Woolley, J. Chem. Soc. Faraday Trans. 1 **75**, 2678 (1979).

[5] L. T. Cowley, D. J. Waddington, and A. Woolley, J. Chem. Soc. Faraday Trans. 1 **78**, 2535 (1982).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

[7] J. E. Bennett, D. M. Brown, and B. Mile, Trans. Faraday Soc. **66**, 386 (1970).

$$CH_3COCH_2O_2 + CH_3COCH_2O_2 \rightarrow CH_3COCH_2OH + CH_3COCHO + O_2 \quad (1)$$

$$\rightarrow 2CH_3COCH_2O + O_2 \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.0\pm0.2)\times10^{-12}$	298	Bridier *et al.*, 1993[1]	(a), (b)
$<8.3\times10^{-12}$	298	Cox *et al.*, 1990[2]	PR-UVA (c)
Branching Ratios			
$k_2/k=0.75\pm0.1$	298	Bridier *et al.*, 1993[1]	(d)
Reviews and Evaluations			
8.0×10^{-12}	298	IUPAC, 1997[3]	(e)

Comments

(a) k is defined by $-d[CH_3COCH_2O_2]/dt = 2k[CH_3COCH_2O_2]^2$.

(b) Flash photolysis of Cl_2 in the presence of CH_3COCH_3–N_2 mixtures at a total pressure of 1 bar. The rate coefficient k was derived from a kinetic analysis of absorption–time profiles at 230 and 260 nm, taking account of the information on the mechanism of the overall reaction obtained from the product study of Jenkin *et al.*[4]

(c) Derived value of $k_{obs}=(8.3\pm1.6)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K is an upper limit due to secondary reactions producing possible enhanced decay of $CH_3COCH_2O_2$ radicals.

(d) Same experiments as for comment (a). The branching ratio was obtained on the basis of absorption due to radicals formed in reaction (2) and subsequent reactions.

(e) See Comments on Preferred Values.

Preferred Values

$k = 8.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.75$ at 298 K.

Reliability

$\Delta \log k = \pm0.3$ at 298 K.
$\Delta(k_2/k) = \pm0.1$ at 298 K.

Comments on Preferred Values

The rate coefficient for $CH_3COCH_2O_2$ radical decay obtained in the two studies[1,2] is in good agreement and the more rigorous analysis carried out by Bridier *et al.*[1] on the basis of the product study of Jenkin *et al.*[4] provides the basis for the recommendation. The recommendations on the overall rate coefficient and the branching ratio at 298 K, which are identical to those in our previous evaluation, IUPAC, 1997,[3] require independent verification.

References

[1] I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. **89**, 2993 (1993).

[2] R. A. Cox, J. Munk, O. J. Nielsen, P. Pagsberg, and E. Ratajczak, Chem. Phys. Lett. **173**, 206 (1990).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

[4] M. E. Jenkin, R. A. Cox, M. Emrich, and G. K. Moortgat, J. Chem. Soc. Faraday Trans. **89**, 2983 (1993).

$$\mathrm{RCHOO + O_3 \rightarrow RCHO + 2O_2} \quad (1)$$

$$\mathrm{RCHOO + H_2O \rightarrow products} \quad (2)$$

$$\mathrm{RCHOO + CO \rightarrow products} \quad (3)$$

$$\mathrm{RCHOO + HCHO \rightarrow products} \quad (4)$$

$$\mathrm{RCHOO + C_2H_4 \rightarrow products} \quad (5)$$

$$\mathrm{RCHOO + NO \rightarrow RCHO + NO_2} \quad (6)$$

$$\mathrm{RCHOO + NO_2 \rightarrow RCHO + NO_3} \quad (7)$$

$$\mathrm{RCHOO + SO_2 \rightarrow products} \quad (8)$$

$$\mathrm{RCHOO + HCOOH \rightarrow products} \quad (9)$$

$$(\mathrm{R = H\ or\ CH_3})$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Biradical	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients				
$k_2/k_8=(6.1\pm0.3)\times10^{-5}$	CH_3CHOO	295	Calvert *et al.*, 1978[1]	(a)
$k_1:k_3:k_4:k_5:k_8=2.5\times10^{-3}:1.8\times10^{-3}:2.5\times10^{-1}:2.5\times10^{-3}:1.0$	CH_2OO	296	Su, Calvert, and Shaw, 1980[2]	RR-FTIR (b)
$k_2/k_8=(2.3\pm1)\times10^{-4}$	CH_2OO	298	Suto, Manzanares, and Lee, 1984[3]	(c)
$k_7/k_8=(1.4\pm0.4)\times10^{-2}$	CH_2OO	298	Manzanares, Suto, and Lee, 1987[4]	(d)
$k_2/k_8=(8.3\pm3.6)\times10^{-4}$	CH_2OO	298	Becker, Bechara, and Brockmann, 1993[5]	RR-FTIR/TDLS (e)
$k_2/k_8=(4.1\pm2.2)\times10^{-4}$	$(CH_3)_2COO$	298	Becker, Bechara, and Brockmann, 1993[5]	RR-FTIR/TDLS (f)
$k_2/k_9=7.1\times10^{-5}$	CH_2OO	298	Neeb *et al.*, 1997[6]	RR-FTIR/HPLC (g)
Reviews and Evaluations				
$k_2=2\times10^{-19}$ to 1×10^{-15}	CH_2OO	298	Herron, Martinez, and Huie, 1982[7]	(h)
$k_4=2\times10^{-16}$ to 8×10^{-13}	CH_2OO	298		(i)
$k_7=1\times10^{-17}$ to 7×10^{-14}	CH_2OO/CH_3CHOO	298		(j)
$k_8=3\times10^{-15}$ to 1.7×10^{-11}	CH_2OO/CH_3CHOO	298		(k)
$k_2:k_3:k_4:k_6:k_7:k_8=5\times10^{-3}:2\times10^{-3}:0.25:10^2:10:1$	CH_2OO/CH_3CHOO	298	Atkinson and Lloyd, 1984[8]	(l)
$k_2\sim4\times10^{-18}$	CH_2OO/CH_3CHOO	298		(m)
$k_4\sim2\times10^{-14}$	CH_2OO/CH_3CHOO	298		(n)
$k_6=7\times10^{-12}$	CH_2OO/CH_3CHOO	298		(o)
$k_7\sim7\times10^{-13}$	CH_2OO/CH_3CHOO	298		(m)
$k_8\sim7\times10^{-14}$	CH_2OO/CH_3CHOO	298		(m)
$k_2=4\times10^{-16}$	CH_2OO	298	Kerr and Calvert, 1984[9]	(o)
$k_3=1.3\times10^{-14}$	CH_2OO	298		(o)
$k_4=2\times10^{-12}$	CH_2OO	298		(o)
$k_6=7\times10^{-12}$	CH_2OO/CH_3CHOO	298		(o)
$k_7=1.0\times10^{-13}$	CH_2OO/CH_3CHOO	298		(o)
$k_8=7\times10^{-12}$	CH_2OO	298		(o)

Comments

(a) Derived from a reanalysis of the data of Cox and Penkett[10] from a study of the aerosol formation from SO_2 in the presence of O_3–O_2–*cis*-2-C_4H_8 mixtures at atmospheric pressure. In this system the biradical intermediate involved is believed to be $CH_3\dot{C}HO\dot{O}$.

(b) FTIR study of the C_2H_4–O_3 reaction in the presence of O_2–N_2 mixtures at a total pressure of 920 mbar and with added CO, HCHO, or SO_2. Relative rate coefficients derived from a computer simulation of reactant consumption and product formation, based on a mechanism of 20 elementary reactions.

(c) Flow system involving C_2H_4–O_3–SO_2–H_2O mixtures in which H_2SO_4 aerosol concentrations were monitored by scattered UV light. Relative rate coefficients obtained from the dependencies of the aerosol formation on the concentrations of O_3, SO_2, and H_2O.

(d) Similar study to that of comment (c), with the inclusion of the effect of added NO_2 on the formation of the H_2SO_4 aerosol.

(e) Study of the C_2H_4–O_3 reaction in the presence of 1 bar of synthetic air with and without added SO_2; H_2O_2 yields were measured by tunable diode laser absorption spectroscopy or by FTIR spectroscopy.

(f) Same study as for comment (e) with $(CH_3)_2C{=}C(CH_3)_2$ as the reactant.

(g) Reaction carried out in a 570 L spherical glass reactor. Hydroxmethyl hydroperoxide (HMHP) concentrations monitored by HPLC and formic acid concentration by FTIR. Formation of HCOOH from HMHP shown to be due, in part, to heterogeneous processes. k_2/k_9 was derived by fitting [HCOOH] and [HMHP] as a function of time to a reaction scheme and using values of $k(O_3+C_2H_4)=1.6\times10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}, $k(CH_3OO+H_2O)=1\times10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} and assuming that 47% of the Criegee biradicals are stabilized.

(h) Based on the ratio $k_2/k_8\approx6\times10^{-5}$, as derived by Calvert *et al.*[1] from the data of Cox and Penkett,[10] and taking $3\times10^{-15}<k_8<1.7\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [see comment (l)].

(i) Based on a study of the ozonide formation in the system O_3–O_2–*cis*-2-C_4H_8–HCHO by Niki *et al.*[11] and on thermochemical kinetic estimates of Nangia and Benson.[12] Details were not provided. It has been assumed that the reactivities of the $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$ biradicals are identical.

(j) Derived from the ratio $k_4/k_7\approx14$, which has been estimated from the data of Martinez *et al.*[13] from a study of the reduction in secondary ozonide formation from the O_3–O_2–*trans*-2-C_4H_8 reaction in the presence of NO_2. k_7 was calculated by taking 2×10^{-16} cm^3 $molecule^{-1}$ $s^{-1}<k_4<8\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} [see comment (i)]. It has been assumed that the reactivities of the $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$ biradicals are identical.

(k) Based on the suppression of ozonide formation in the O_3–O_2–*cis*-2-C_4H_8–HCHO system by SO_2 observed by Niki *et al.*[11] and on thermochemical kinetic estimates of Nangia and Benson.[12] Details were not provided. It has been assumed that the reactivities of the $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$ biradicals are identical.

(l) The relative rate coefficients are proposed on the basis that the data on $\dot{C}H_2O\dot{O}$ (Su *et al.*[2]) and on $CH_3\dot{C}HO\dot{O}$ (Cox and Penkett[10]) can be amalgamated, i.e., $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$ have the same reactivities. From the studies of Akimoto *et al.*[14,15] on the O_3–C_2H_4 and C_3H_6 system, it was estimated that $k_6:k_7:k_8=10^2:10:1$.

(m) Calculated from the above relative rate coefficients and assuming that $k_6=7\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} [see comment (n)].

(n) This rate coefficient was assumed to have a value similar to that for the reaction of alkylperoxy radicals with NO ($RO_2+NO\rightarrow RO+NO_2$), and hence $k_6=7\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

(o) Calculated (i) on the assumption that $k_6=k_8$ and taking the estimated value of $k_6=7\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} of Atkinson and Lloyd[8] and (ii) from the relative rate data of Calvert *et al.*,[1] Su *et al.*,[2] and Suto *et al.*[3]

Preferred Values

No recommendation.

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation, IUPAC, 1997.[16] Vibrationally excited Criegee intermediates or biradicals, $[R\dot{C}HO\dot{O}]^\ddagger$, are produced from the reactions of O_3 with alkenes.[17] These species decompose unimolecularly to give molecular or radical products or undergo collisional deactivation to yield thermally equilibrated biradicals, $R\dot{C}HO\dot{O}$. Here we consider the kinetic and other information relating to the bimolecular reactions that have been proposed for these thermally equilibrated biradicals.

Studies have been made of the reactions of $R\dot{C}HO\dot{O}$ with aldehydes,[2,10,18-22] SO_2,[1,2,9,10,23] . H_2O,[10,14,24] carboxylic acids,[22,25] and methanol,[25] but detailed kinetic data are often lacking. Relative rate coefficients have been derived by Calvert *et al.*,[1] Su *et al.*,[2] and Suto *et al.*,[3] based on experimental measurements of the rates of consumption of molecular reactants relative to consumption of SO_2 in systems involving $R\dot{C}HO\dot{O}$ biradicals. The only compound, other than SO_2, common to any of these studies is H_2O, for which the derived relative rate coefficients differ by a factor of ~4. Notwithstanding this discrepancy, these relative rate measurements are the only experimental basis on which to assess the rates of these reactions. It is apparent from these measurements that the reactions of the biradicals $R\dot{C}HO\dot{O}$ with O_3, CO, and alkenes are not important under atmospheric conditions. The reactions with H_2O, RCHO, NO_2, and SO_2 need to be considered, although for most tropospheric conditions the only effective reaction of the biradicals is likely to be that with H_2O.

Previous reviewers[8,9] have made the reasonable assumption that the reaction of $R\dot{C}HO\dot{O}$ with NO could also be significant, based on estimates of the energetics of the proposed reaction pathway $R\dot{C}HO\dot{O}+NO\rightarrow RCHO+NO_2$. Unfortunately, there is no direct experimental evidence for this reaction and very little information upon which to base an estimate of its rate coefficient. Atkinson and Lloyd[8] have estimated the relative rate coefficients for $R\dot{C}HO\dot{O}$ reacting with NO and SO_2, corresponding to $k_6/k_8=10^2$, whereas Kerr and Calvert[9] propose $k_6/k_8=1$. Experimental data on this ratio of rate coefficients are badly needed.

In the absence of direct kinetic measurements of the absolute rate coefficients of any of the $R\dot{C}HO\dot{O}$ bimolecular reactions, both Atkinson and Lloyd[8] and Kerr and Calvert[9] have suggested that k_6 should be equated to the rate coefficient for the structurally analogous reactions, $RO_2+NO\rightarrow RO+NO_2$, with $k_6=7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K. While this seems a reasonable proposition, it is desirable to obtain experimental verification. At present it is difficult to see how any direct measurements could be made with $R\dot{C}HO\dot{O}$ systems involving O_3–alkene reactions owing to the complex chemistry involved. In this regard the study of Hatakeyama *et al.*[24] involving the generation of CH_2OO biradicals from the reaction of $CH_2(^3B_1)$ with O_2 are of considerable interest.

In deriving the relative rate coefficients listed above, it has been necessary in some cases to compare data obtained from different O_3–alkene systems and to assume that all the $R\dot{C}HO\dot{O}$ biradicals have equal reactivity, e.g., $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$. Again, while this seems to be a reasonable assumption, it requires experimental verification.

There is little direct experimental evidence on the products of the reactions (1)–(9). Where the products are stated these have largely been suggested on the basis of analogy with related reactions.

Recent work of Neeb *et al.*[26] suggests that the reaction of the $\dot{C}H_2O\dot{O}$ biradical with H_2O leads initially to hydroxymethyl hydroperoxide ($HOCH_2OOH$). The $HOCH_2OOH$ may then decompose to HCOOH and H_2O but the extent to which this occurred by heterogeneous processes in the system used by Neeb *et al.*[26] is uncertain. Hydroperoxides have been found in a number of other O_3–alkene studies[27–29] and are suggested to arise in a similar way, by direct interaction of the Criegee biradical with H_2O,

$$R_1R_2\dot{C}O\dot{O}+H_2O\rightarrow R_1R_2C(OH)OOH.$$

In addition to the expected formation of carboxylic acids from the reactions of the biradicals with H_2O,

$$R\dot{C}HO\dot{O}+H_2O\rightarrow RCOOH+H_2O,$$

recent studies of the reactions of O_3 with *trans*-2-butene,[5,27,30] isoprene,[27,30] and monoterpenes[27,30] have reported varying amounts of H_2O_2 product. Since the yields of H_2O_2 were considerably enhanced by the presence of H_2O, it was proposed that H_2O_2 was formed in a direct reaction involving Criegee biradicals:

$$R_1R_2\dot{C}O\dot{O}+H_2O\rightarrow(R_1R_2COO\cdot H_2O)$$

$$(R_1R_2COO\cdot H_2O)\rightarrow R_1COR_2+H_2O_2.$$

For $\dot{C}H_2O\dot{O}$ a possible reaction sequence with H_2O is

$$\dot{C}H_2O\dot{O}+H_2O\rightarrow HCHO+H_2O_2$$

$$\rightarrow[HOCH_2OOH]\xrightarrow{M}HOCH_2OOH$$

$$\downarrow$$

$$HCOOH+H_2O$$

with the reaction leading to H_2O_2 being a minor pathway. The degree of stability of the $HOCH_2OOH$ is uncertain. It may also decompose into $HCOOH+H_2O$.

Reaction of $R_1R_2\dot{C}O\dot{O}$ biradicals with aldehydes leads to the formation of the corresponding ozonides,[11,31,32] i.e., $R_1R_2\dot{C}O\dot{O}+R_3CHO\rightarrow R_1R_2COOCH(O)R_3$. However, the formation of ethene ozonide has not been observed in the reaction of $\dot{C}H_2O\dot{O}$ with HCHO or in the O_3–ethene reaction.[2,19,21,32] The proposal that the reaction of the $\dot{C}H_2O\dot{O}$ biradical with HCHO leads to $HOCH_2OCHO$[2,19,21,32,33] has now been shown to be incorrect. The spectrum observed in the $\dot{C}H_2O\dot{O}$–HCHO reaction and assigned to $HOCH_2OCHO$ is now known to belong to $HOOCH_2OCHO$,[34,35] which can be formed by the reaction of the $\dot{C}H_2O\dot{O}$ biradical with HCOOH.

References

[1] J. G. Calvert, F. Su, J. W. Bottenheim, and O. P. Strausz, Atmos. Environ. **12**, 197 (1978).

[2] F. Su, J. G. Calvert, and J. H. Shaw, J. Phys. Chem. **84**, 239 (1980).

[3] M. Suto, E. R. Manzanares, and L. C. Lee, Environ. Sci. Technol. **19**, 815 (1985).

[4] E. R. Manzanares, M. Suto, and L. C. Lee (unpublished data).

[5] K. H. Becker, J. Bechara, and K. J. Brockmann, Atmos. Environ. **27A**, 57 (1993).

[6] P. Neeb, F. Sauer, O. Horie, and G. Moortgat, Atmos. Environ. **31**, 1417 (1997).

[7] J. T. Herron, R. I. Martinez, and R. E. Huie, Int. J. Chem. Kinet. **14**, 201 (1982).

[8] R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).

[9] J. A. Kerr and J. G. Calvert, *Chemical Transformation Modules for Eulerian Acid Deposition Models*. The Gas-Phase Chemistry, Volume I (National Center for Atmospheric Research, Boulder, CO, 1984).

[10] R. A. Cox and S. A. Penkett, J. Chem. Soc. Faraday Trans. 1 **68**, 1735 (1972).

[11] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Chem. Phys. Lett. **46**, 327 (1977).

[12] P. S. Nangia and S. W. Benson, Int. J. Chem. Kinet. **12**, 43 (1980).

[13] R. I. Martinez, R. E. Huie, and J. T. Herron, Chem. Phys. Lett. **72**, 443 (1980).

[14] H. Akimoto, H. Bandow, F. Sakamaki, G. Inoue, M. Hoshino, and M. Okuda, Research Report No. 9, R-9-79, National Institute for Environmental Studies, Japan (1979).

[15] H. Akimoto, H. Bandow, F. Sakamaki, G. Inoue, M. Hoshino, and M. Okuda, Environ. Sci. Technol. **14**, 172 (1980).

[16] IUPAC, Supplement V, 1997 (see references in Introduction).

[17] R. Atkinson and W. P. L. Carter, Chem. Rev. **84**, 437 (1984).

[18] P. L. Hanst, E. R. Stephens, W. E. Scott, and R. C. Doerr, *Atmospheric Ozone-Olefin Reactions* (Franklin Institute, Philadelphia, PA, 1958).

[19] C. S. Kan, F. Su, J. G. Calvert, and J. H. Shaw, J. Phys. Chem. **85**, 2359 (1981).

[20] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, presented at the International Conference on Environmental Sensing and Assessment, Las Vegas, NV, 1915, Vol. 2, p. 24-4.

[21] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **85**, 1024 (1981).

[22] P. Neeb, O. Horie, and G. K. Moortgat, Chem. Phys. Lett. **246**, 150 (1995).

[23] S. Hatakeyama, H. Kobayashi, Z.-Y. Lin, H. Takagi, and H. Akimoto, J. Phys. Chem. **90**, 4131 (1986).

[24] S. Hatakeyama, H. Bandow, M. Okuda, and H. Akimoto, J. Phys. Chem. **85**, 2249 (1981).

[25] P. Neeb, O. Horie, and G. K. Moortgat, Int. J. Chem. Kinet. **28**, 721 (1996).

[26] P. Neeb, F. Sauer, O. Horie, and G. K. Moortgat, Atmos. Environ. **31**, 1417 (1997).
[27] R. Simonaitis, K. J. Olszyna, and J. F. Meagher, Geophys. Res. Lett. **18**, 9 (1991).
[28] R. I. Martinez, J. T. Herron, and R. E. Huie, J. Am. Chem. Soc. **103**, 3807 (1981).
[29] S. Gäb, E. Hellpointer, W. V. Turner, and F. Kórte, Nature (London) **316**, 535 (1985).
[30] K. H. Becker, K. J. Brockmann, and J. Bechara, Nature (London) **346**, 256 (1990).
[31] H. Niki, P. D. Maker, C. M. Savage, L. P. Breitenbach, and D. M. Hurley, J. Phys. Chem. **91**, 941 (1987).
[32] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Environ. Sci. Technol. **17**, 312A (1983).
[33] O. Horie and G. K. Moortgat, Atmos. Environ. **25A**, 1881 (1991).
[34] P. Neeb, O. Horie, and G. K. Moortgat, Chem. Phys. Lett. **246**, 150 (1995).
[35] J. Thamm, S. Wolff, W. V. Turner, S. Gäb, W. Thomas, F. Zabel, E. H. Fink, and K. H. Becker, Chem. Phys. Lett. **258**, 155 (1996).

$O_3 + C_2H_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.8\pm1.2)\times10^{-21}$	294	Atkinson and Aschmann, 1984[1]	S-CL (a)
Reviews and Evaluations			
$1.0\times10^{-14}\exp(-4100/T)$	~298	NASA, 1997[2]	(b)
1×10^{-20}	298	IUPAC, 1997[3]	(c)

Comments

(a) Static system, with $[O_3]$ being monitored by chemiluminescence in large excess of C_2H_2 at a total pressure of 980 mbar.

(b) The 298 K rate coefficient was based on the measured value of Atkinson and Aschmann[1] and is identical to the present IUPAC recommendation. The temperature dependence was estimated.

(c) See Comments on Preferred Values.

Preferred Values

$k=1\times10^{-20}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k=\pm1.0$ at 298 K.

Comments on Preferred Values

The literature data at room temperature[1,4–8] exhibit a large degree of scatter covering the range $k(298\text{ K})=(0.78-7.8)\times10^{-20}$ cm^3 molecule^{-1} s^{-1}. The preferred value at 298 K is based upon the value obtained by Atkinson and Aschmann.[1] This is the most recent study; it gives the lowest of the values so far obtained and is likely to be the most accurate (any impurities are likely to lead to higher values).

There has been one study of the temperature dependence of the rate coefficient[5] giving a value of $E/R=5435$ over the temperature range 243–283 K. However, in view of the difficulties in studying this reaction and the small temperature range covered, no recommendation is made for the temperature dependence.

A large uncertainty is assigned to the preferred value at 298 K to encompass the wide scatter in the results. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[3]

References

[1] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **16**, 259 (1984).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).
[4] R. D. Cadle and C. Schadt, J. Phys. Chem. **21**, 163 (1953).
[5] W. B. DeMore, Int. J. Chem. Kinet. **1**, 209 (1969).
[6] W. B. DeMore, Int. J. Chem. Kinet. **3**, 161 (1971).
[7] D. H. Stedman and H. Niki, Environ. Lett. **4**, 303 (1973).
[8] C. T. Pate, R. Atkinson, and J. N. Pitts, Jr., J. Environ. Sci. Health **A11**, 1 (1976).

$O_3 + C_2H_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$3.3\times10^{-15}\exp[-(2365\pm101)/T]$	178–233	DeMore, 1969[1]	S-UVA (a)
1.18×10^{-18}	298*		
$(1.55\pm0.15)\times10^{-18}$	299	Stedman, Wu, and Niki, 1973[2]	S-CL (b)
$9.00\times10^{-15}\exp[-(2557\pm167)/T]$	235–362	Herron and Huie, 1974[3]	(c)
1.69×10^{-18}	298		
$(1.9\pm0.1)\times10^{-18}$	299	Japar, Wu, and Niki, 1974[4]	S-CL (b)
$(1.9\pm0.1)\times10^{-18}$	299	Japar, Wu, and Niki, 1976[5]	S-CL (b)
$(1.69\pm0.13)\times10^{-18}$	303	Toby, Toby, and O'Neal, 1976[6]	S-UVA (a)
$(1.43\pm0.19)\times10^{-18}$	296	Atkinson *et al.*, 1982[7]	S-CL (b)
$7.72\times10^{-15}\exp[-(2557\pm30)/T]$	232–298	Bahta, Simonaitis, and Heicklen, 1984[8]	S-UVA (a)
$(1.45\pm0.10)\times10^{-18}$	298		
$5.1\times10^{-15}\exp[-(2446\pm91)/T]$	240–324	Treacy *et al.*, 1992[9]	S-CL (b)
$(1.37\pm0.08)\times10^{-18}$	298		
Reviews and Evaluations			
$9.14\times10^{-15}\exp(-2580/T)$	178–362	Atkinson, 1997[10]	(d)
$1.2\times10^{-14}\exp(-2630/T)$	180–360	NASA, 1997[11]	(e)
$9.1\times10^{-15}\exp(-2580/T)$	180–360	IUPAC, 1997[12]	(e)

Comments

(a) Static system, with UV absorption detection of O_3 at 253.7 nm.
(b) Static system with chemiluminescence detection of O_3.
(c) Stopped-flow system with MS detection of O_3. Carried out at a total pressure of ~5 mbar but with sufficient O_2 present to minimize the occurrence of secondary reactions removing O_3.
(d) Based on a least-squares analysis of the rate coefficients of DeMore,[1] Stedman *et al.*,[2] Herron and Huie,[3] Japar *et al.*,[4,5] Toby *et al.*,[6] Atkinson *et al.*,[7] Bahta *et al.*,[8] and the 298 K rate coefficient of Treacy *et al.*[9]
(e) Based on the rate coefficient data of DeMore,[1] Stedman *et al.*,[2] Herron and Huie,[3] Japar *et al.*,[4,5] Toby *et al.*,[6] Su *et al.*,[13] Adeniji *et al.*,[14] Kan *et al.*,[15] Atkinson *et al.*,[7] and Bahta *et al.*,[8]

Preferred Values

$k = 1.6\times10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.1\times10^{-15}\exp(-2580/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 180–360 K.

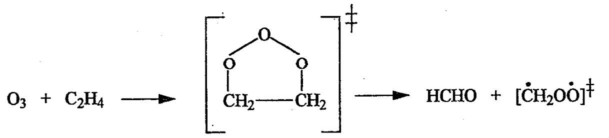
Reliability

$\Delta \log k = \pm0.10$ at 298 K.
$\Delta(E/R) = \pm100$ K.

Comments on Preferred Values

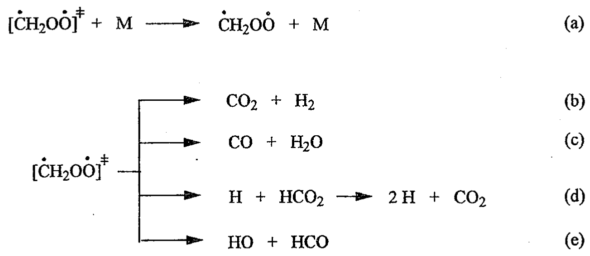
The most recent kinetic studies of Bahta *et al.*[8] and Treacy *et al.*[9] are in good agreement. They give rate coefficients[8,9] that are somewhat lower than many of the previous determinations, including those of Su *et al.*[13] and Kan *et al.*,[15] which are not used in this evaluation. Since Treacy *et al.*[9] did not tabulate the individual rate coefficients at the various temperatures studied, only their 298 K values can be used in the evaluation of the rate coefficient for this reaction. The preferred values are obtained from a least-squares analysis of the rate coefficients of DeMore,[1] Stedman *et al.*,[2] Herron and Huie,[3] Japar *et al.*,[4,5] Toby *et al.*,[6] Atkinson *et al.*,[7] Bahta *et al.*[8] (averaging the rate coefficients at each of the four temperatures studied), and the 298 K rate coefficient of Treacy *et al.*[9] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[12]

As discussed by Atkinson and Lloyd,[16] Atkinson and Carter,[17] and Atkinson,[10,18] the initial reaction forms the energy-rich trioxane which rapidly decomposes:



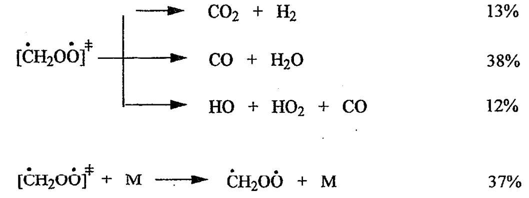
to yield HCHO and the energy-rich biradical $[\dot{C}H_2O\dot{O}]^\ddagger$. Grosjean and Grosjean[19] and Grosjean *et al.*[20] have obtained a formation yield of unity for HCHO.

The energy-rich biradical can either be stabilized or decompose. The decomposition channels (b)–(e) have been postulated.



There have been a number of determinations of the yield of stabilized biradicals. The values obtained for room temperature and atmospheric pressure by Su *et al.*[13] (0.35 ±0.05), Kerr *et al.*[15] (0.37±0.02), Niki *et al.*[21] (0.35 ±0.05), and Hatakeyama *et al.*[22,23] (0.390±0.053) are in good agreement and are preferred to the slightly higher value of 0.47 obtained by Horie and Moortgat.[24] The yield of stabilized biradicals is pressure dependent although a significant fraction appear to be formed thermally "cold" at low pressures. By extrapolation of measurements over the range 13 mbar–1.5 bar, Hatakeyama *et al.*[23] found this fraction to be 0.20±0.03 at zero pressure.

On the basis of the work of Herron and Huie,[26] Su *et al.*,[13] and Horie and Moortgat[24] the fractions of the overall reaction proceeding by the decomposition channels (b)–(d) at room temperature and atmospheric pressure are approximately 0.13, 0.31–0.58, and 0.06–0.10, respectively.[18] However, Atkinson *et al.*[25] have also observed the formation of HO radicals at room temperature and atmospheric pressure of air, with a yield of ~0.12. The observed formation of HO radicals,[25] presumably via pathway (e), probably indicates that pathway (c) does not occur, since the study of Herron and Huie[26] could not differentiate between formation of H atoms and HO radicals (any H atoms formed would rapidly react with O_3 in the reaction system used by Herron and Huie[26] to produce HO radicals). Hence a possible reaction sequence is



The relative importance of these decomposition/stabilization reactions of the $[\dot{C}H_2O\dot{O}]^\ddagger$ radical are, however, pressure dependent,[23] with no quantitative data being available other than at ~1 bar of air.

References

[1] W. B. DeMore, Int. J. Chem. Kinet. **1**, 209 (1969).
[2] D. H. Stedman, C. H. Wu, and H. Niki, J. Phys. Chem. **77**, 2511 (1973).
[3] J. T. Herron and R. E. Huie, J. Phys. Chem. **78**, 2085 (1974).
[4] S. M. Japar, C. H. Wu, and H. Niki, J. Phys. Chem. **78**, 2318 (1974).
[5] S. M. Japar, C. H. Wu, and H. Niki, J. Phys. Chem. **80**, 2057 (1976).
[6] F. S. Toby, S. Toby, and H. E. O'Neal, Int. J. Chem. Kinet. **8**, 25 (1976).
[7] R. Atkinson, S. M. Aschmann, D. R. Fitz, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **14**, 13 (1982).
[8] A. Bahta, R. Simonaitis, and J. Heicklen, Int. J. Chem. Kinet. **16**, 1227 (1984).
[9] J. Treacy, M. El Hag, D. O'Farrell, and H. Sidebottom, Ber. Bunsenges. Phys. Chem. **96**, 422 (1992).
[10] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).
[11] NASA Evaluation No. 12, 1997 (see references in Introduction).
[12] IUPAC, Supplement V, 1997 (see references in Introduction).
[13] F. Su, J. G. Calvert, and J. H. Shaw, J. Phys. Chem. **84**, 239 (1980).
[14] S. A. Adeniji, J. A. Kerr, and M. R. Williams, Int. J. Chem. Kinet. **13**, 209 (1981).
[15] C. S. Kan, F. Su, J. G. Calvert, and J. H. Shaw, J. Phys. Chem. **85**, 2359 (1981).
[16] R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).
[17] R. Atkinson and W. P. L. Carter, Chem. Rev. **84**, 437 (1984).
[18] R. Atkinson, J. Phys. Chem. Ref. Data **Monograph 2**, 1 (1994).
[19] E. Grosjean and D. Grosjean, Environ. Sci. Technol. **30**, 2036 (1996).
[20] E. Grosjean, J. B. Andrade, and D. Grosjean, Eviron. Sci. Technol. **30**, 975 (1996).
[21] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **85**, 1024 (1981).
[22] S. Hatakeyama, H. Kobayashi, and H. Akimoto, J. Phys. Chem. **88**, 4736 (1984).
[23] S. Hatakeyama, H. Kobayashi, Z.-Y. Lin, H. Takagi, and H. Akimoto, J. Phys. Chem. **90**, 4131 (1986).
[24] O. Horie and G. K. Moortgat, Atmos. Environ. **25A**, 1881 (1991).
[25] R. Atkinson, S. M. Aschmann, J. Arey, and B. Shorees, J. Geophys. Res. **97**, 6065 (1992).
[26] J. T. Herron and R. E. Huie, J. Am. Chem. Soc. **99**, 5430 (1977).

$O_3 + C_3H_6 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$6.14 \times 10^{-15} \exp[-(1897 \pm 109)/T]$	235–362	Herron and Huie, 1974[1]	(a)
1.06×10^{-17}	298		
$4.9 \times 10^{-15} \exp[-(1858 \pm 70)/T]$	240–324	Treacy *et al.*, 1992[2]	S-CL (b)
$(9.4 \pm 0.4) \times 10^{-18}$	298		
Reviews and Evaluations			
$5.51 \times 10^{-15} \exp(-1878/T)$	235–362	Atkinson, 1997[3]	(c)
$6.5 \times 10^{-15} \exp(-1900/T)$	235–360	NASA, 1997[4]	(d)
$5.5 \times 10^{-15} \exp(-1880/T)$	230–370	IUPAC, 1997[5]	(e)

Comments

(a) Stopped-flow system, with MS detection of O_3. Carried out at a total pressure of ~5 mbar, but with sufficient O_2 present to minimize the occurrence of secondary reactions removing O_3. (Due to a typographical error, the lowest temperature studied was 235.0 K and not 250.0 K as originally stated).

(b) Static system, with chemiluminescence detection of O_3. C_3H_6 in large excess over O_3.

(c) Derived from the absolute rate coefficient data of Herron and Huie[1] and Treacy *et al.*[2]

(d) Based mainly on the absolute rate coefficient data of Herron and Huie.[1]

(e) See Comments on Preferred Values.

Preferred Values

$k = 1.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.5 \times 10^{-15} \exp(-1880/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–370 K.

Reliability

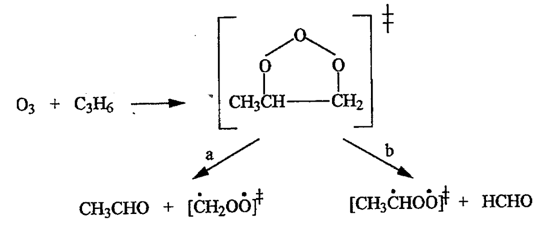
$\Delta \log k = \pm 0.10$ at 298 K.

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

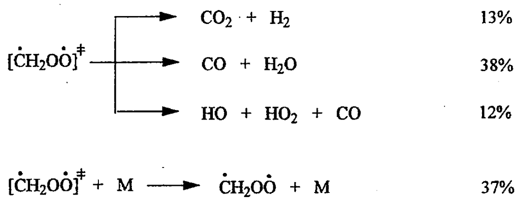
Comments on Preferred Values

The absolute rate coefficients of Herron and Huie[1] (note that the lowest temperature studied was 235.0 K and not 250.0 K as given by Herron and Huie[1]) and Treacy *et al.*[2] are in excellent agreement for propene, 1-butene, *cis*- and *trans*-2-butene, 2-methylpropene and 2-methyl-2-butene over the temperature ranges common to both studies.[3] Accordingly, the 298 K rate coefficients and temperature dependencies of Herron and Huie[1] and Treacy *et al.*[2] have been averaged to yield the preferred Arrhenius expression (note that the individual rate coefficients at the various temperatures studied by Treacy *et al.*[2] were not tabulated). The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

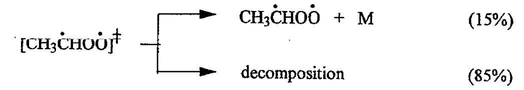
The reaction proceeds via the initial formation of a trioxane, which rapidly decomposes:



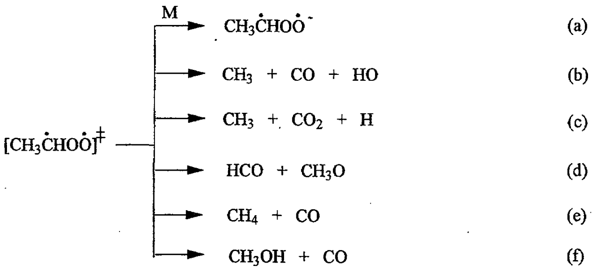
For 1-alkenes measured product yields suggest that the two primary carbonyls are formed in essentially equal yields, i.e., $k_a \approx k_b$.[6] For propene, the CH_3CHO primary yields of 0.520 ± 0.026 and 0.446 ± 0.092 have been obtained by Grosjean *et al.*[6] and Tuazon *et al.*,[7] respectively. Higher yields of HCHO were obtained by both groups, but these include contributions from subsequent reactions of the $CH_3\dot{C}HO\dot{O}$ biradicals. It is generally assumed[8,9] that the reactions of the energy-rich biradical $[\dot{C}H_2O\dot{O}]^{\ddagger}$ formed from propene are similar to those for $[\dot{C}H_2O\dot{O}]^{\ddagger}$ formed from ethene. Hence, as for the $O_3 + C_2H_4$ reaction at room temperature and 1 bar of air



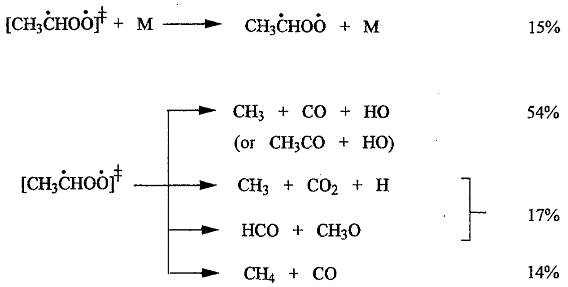
Less data are available concerning the stabilization and decomposition reactions of the $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ biradical. Based upon the SO_2 to H_2SO_4 conversion yield in an O_3+propene reaction system, Hatakeyama *et al.*[10] determined an overall stabilized biradical ($\dot{C}H_2O\dot{O} + CH_3\dot{C}HO\dot{O}$) yield of 0.254 ± 0.023 at room temperature and atmospheric pressure, while Horie and Moortgat[11] obtained a stabilized biradical yield of 0.44. Using the data of Hatakeyama *et al.*[10] and assuming that $k_a = k_b$ and that the $[\dot{C}H_2O\dot{O}]^{\ddagger}$ stabilization yield is 0.37, then the fraction of $[CH_3\dot{C}HO\dot{O}]^‡$ biradicals which are stabilized at ~298 K and 1 bar of air is 0.14. While the stabilization/decomposition yields are expected to depend on the individual alkene reacting with O_3 (and on the total pressure and temperature), this fraction of $[CH_3\dot{C}HO\dot{O}]$ biradicals which are stabilized at 298 K and 1 bar of air is similar to the measured yields of stabilized $CH_3\dot{C}HO\dot{O}$ from *trans*-2-butene (0.185[10]) and *cis*-2-butene (0.18[12]). A yield of stabilized $CH_3\dot{C}HO\dot{O}$ from $[CH_3\dot{C}HO\dot{O}]^‡$ of 0.15 at 298 K and 1 bar of air is recommended, consistent with the product data of Hatakeyama *et al.*:[10]



The decomposition pathways are less well understood,[6,8,9] but are expected to involve formation of $CH_3+CO+OH$, CH_3+CO_2+H, $HCO+CH_3O$, CH_4+CO_2, and CH_3OH+CO.



Recent studies and evaluations[5,6] conclude that these channels have approximate fractional overall yields at ~1 bar of air of: channel (a), 0.15–0.42; channel (b), 0.16–0.30; channel (c), 0.17–0.34; channel (d), 0–0.07; channel (e), 0.14–0.17; and channel (f), 0–0.07. However, Atkinson and Aschmann[13] have observed the formation of OH radicals from the ozone reaction with propene at room temperature and atmospheric pressure of air, with a yield of 0.33 (uncertain to a factor of ~1.5). A possible reaction sequence for the $[CH_3\dot{C}HO\dot{O}]^‡$ biradical at 298 K and 1 bar air is



References

[1] J. T. Herron and R. E. Huie, J. Phys. Chem. **78**, 2085 (1974).
[2] J. Treacy, M. El Hag, D. O'Farrell, and H. Sidebottom, Ber. Bunsenges. Phys. Chem. **96**, 422 (1992).
[3] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).
[4] NASA Evaluation No. 12, 1997 (see references in Introduction).
[5] IUPAC, Supplement V, 1997 (see references in Introduction).
[6] E. Grosjean, J. B. deAndrade, and D. Grosjean, Environ. Sci. Technol. **30**, 975 (1996).
[7] E. C. Tuazon, S. M. Aschmann, J. Arey, and R. Atkinson, Environ. Sci. Technol. **31**, 3004 (1997).
[8] R. Atkinson and W. P. L. Carter, Chem. Rev. **84**, 437 (1984).
[9] R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).
[10] S. Hatakeyama, H. Kobayashi, and H. Akimoto, J. Phys. Chem. **88**, 4736 (1984).
[11] O. Horie and G. K. Moortgat, Atmos. Environ. **25A**, 1881 (1991).
[12] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Chem. Phys. Lett. **46**, 327 (1977).
[13] R. Atkinson and S. M. Aschmann, Environ. Sci. Technol. **27**, 1357 (1993).

$F + CH_4 \rightarrow HF + CH_3$

$\Delta H° = -131.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
5.5×10^{-10} exp[$-(580\pm150)/T$]	298–450	Wagner, Warnatz, and Zetzsch, 1971[1]	DF-MS
7.9×10^{-11}	298		
7.2×10^{-11}	298	Kompa and Wanner, 1972[2]	(a)
$(6.0\pm6.0)\times10^{-11}$	298	Clyne, McKenney, and Walker, 1973[3]	DF-MS
$(5.72\pm0.30)\times10^{-11}$	298	Fasano and Nogar, 1982[4]	(b)
$(5.3\pm0.3)\times10^{-11}$	294	Moore, Smith, and Stewart, 1994[5]	(c)
Relative Rate Coefficients			
1.1×10^{-10} exp($-187/T$)	253–348	Foon and Reid, 1971[6]	RR (d)
5.9×10^{-11}	298		
1.64×10^{-10} exp($-265/T$)	180–410	Perksy, 1996[7]	RR (e)
$(6.65\pm0.35)\times10^{-11}$	298		
Reviews and Evaluations			
1.6×10^{-10} exp($-260/T$)	180–410	NASA, 1997[8]	(f)
3.0×10^{-10} exp($-400/T$)	250–450	IUPAC, 1997[9]	(g)

Comments

(a) Flash photolysis of WF_6. Overall rate coefficient was obtained by monitoring the decay of the HF chemical laser emission.

(b) Infrared multiphoton dissociation of SF_6 in a mixture of CH_4, D_2, and Ar. First-order decay of [F] was monitored by chemiluminescence from either HF or DF. Dependence of decay rate on mixture composition gave values for k and for $k(F+D_2)$.

(c) Time-resolved vibrational chemiluminescence from HF monitored following the production of F atoms in the presence of CH_4 by pulsed laser photolysis of F_2 at 266 nm. Rate coefficient values were also reported at 218, 179, and 139 K, with the values increasing at temperatures below about 200 K.

(d) Competitive fluorination-consumption technique. Value of k derived from measured ratio $k/k(F+H_2) = 0.82\ \exp(313/T)$ and $k(F+H_2) = 1.4\times10^{-10}\ \exp(-500/T)$ cm^3 molecule^{-1} s^{-1}.[9]

(e) Competitive study using DF-MS technique. Value of k derived from measured ratio $k/k(F+D_2) = 1.21\ \exp(420/T)$, the kinetic isotope effect $k(F+H_2)/k(F+D_2) = 1.04\ \exp(185/T)$,[10] and $k(F+H_2) = 1.4\times10^{-10}\ \exp(-500/T)$ cm^3 molecule^{-1} s^{-1}.[9]

(f) Room temperature value is based on the room temperature values reported in Refs. 1–7. The temperature dependence is from Persky.[7]

(g) Based on the room temperature results of Kompa and Wanner,[2] Clyne *et al.*,[3] and Fasano and Nogar,[4] the 298–450 K results of Wagner *et al.*,[1] and the 253–348 K results of Foon and Reid.[6]

Preferred Values

$k = 6.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.6\times10^{-10}\ \exp(-260/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 180–410 K.

Reliability

$\Delta \log k = \pm0.15$ at 298 K.

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

Comments on Preferred Values

The preferred value at room temperature is based on the room temperature values reported in Wagner *et al.*,[1] Kompa and Wanner,[2] Clyne *et al.*,[3] Fasano and Nogar,[4] Moore *et al.*,[5] Foon and Reid,[6] and Persky.[7] The preferred temperature dependence is that reported by Persky.[7] Results reported in this study are preferred over the temperature dependences reported in the much earlier studies of Wagner *et al.*[1] and Foon and Reid.[6]

References

[1] H. Gg. Wagner, J. Warnatz, and C. Zetzsch, An. Assoc. Quim. Argentina 59, 169 (1971).

[2] K. L. Kompa and J. Wanner, Chem. Phys. Lett. **12**, 560 (1972).

[3] M. A. A. Clyne, D. J. McKenney, and R. F. Walker, Can J. Chem. **51** 3596 (1973).

[4] D. M. Fasano and N. S. Nogar, Chem. Phys. Lett. **92**, 411 (1982).

[5] C. M. Moore, I. W. M. Smith, and D. W. A. Stewart, Int. J. Chem. Kinet **26**, 813 (1994).

[6] R. Foon and G. P. Reid, Trans. Faraday Soc. **67**, 3513 (1971).

[7] A. Persky, J. Phys. Chem. **100**, 689 (1996).

[8] NASA Evaluation No. 12, 1997 (see references in Introduction).

[9] IUPAC, Supplement V, 1997 (see references in Introduction).

[10] A. Persky, J. Chem. Phys. **59**, 3612 (1973).

$Cl + CH_4 \rightarrow HCl + CH_3$

$\Delta H° = 7.6\ kJ \cdot mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$7.94 \times 10^{-12} \exp[-(1260 \pm 35)/T]$	218–401	Watson *et al.*, 1976[1]	FP-RF (a)
$(1.13 \pm 0.1) \times 10^{-13}$	298		
$7.93 \times 10^{-12} \exp[-(1272 \pm 51)/T]$	218–322	Manning and Kurylo, 1977[2]	FP-RF
$(1.04 \pm 0.1) \times 10^{-13}$	296		
$6.51 \times 10^{-12} \exp[-(1229 \pm 27)/T]$	200–299	Whytock *et al.*, 1977[3]	FP-RF (b)
$(1.13 \pm 0.07) \times 10^{-13}$	299		
$(1.08 \pm 0.07) \times 10^{-13}$	298	Michael and Lee, 1977[4]	DF-RF
$1.06 \times 10^{-11} \exp[-(1415 \pm 100)/T]$	268–423	Lin, Leu, and DeMore, 1978[5]	DF-MS
$(9.6 \pm 0.9) \times 10^{-14}$	296		
$8.2 \times 10^{-12} \exp[-(1320 \pm 20/T]$	200–300	Zahniser, Berquist, and Kaufman, 1978[6]	DF-RF (c)
$(9.9 \pm 1.5) \times 10^{-14}$	298		
$7.4 \times 10^{-12} \exp[-(1291 \pm 68)/T]$	220–298	Keyser, 1978[7]	DF-RF (d)
$(1.01 \pm 0.02) \times 10^{-13}$	298		
$3.2 \times 10^{-12} \exp[-(1063 \pm 34)/T]$	221–298	Ravishankara and Wine, 1980[8]	PLP-RF (e)
$(9.65 \pm 0.55) \times 10^{-14}$	298		
$8.06 \times 10^{-12} \exp[-(1300 \pm 113)/T]$	233–338	Heneghan, Knoot, and Benson, 1981[9]	(f)
$(9.60 \pm 0.50) \times 10^{-14}$	298		
$(9.93 \pm 0.13) \times 10^{-14}$	298	Dobis and Benson, 1987[10]	(f)
$(9.17 \pm 0.75) \times 10^{-14}$	294	Sawerysyn *et al.*, 1987[11]	DF-MS
$(9.40 \pm 0.40) \times 10^{-14}$	298	Beichert *et al.*, 1995[12]	DF-RF
$7.0 \times 10^{-12} \exp[-(1270 \pm 60)/T]$	181–291	Seeley, Jayne, and Molina, 1996[13]	(g)
$(9.9 \pm 0.3) \times 10^{-14}$	298*		
$(1.00 \pm 0.10) \times 10^{-13}$	298	Matsumi *et al.*, 1997[14]	PLP-LIF
$3.7 \times 10^{-13}(T/298)^{2.6} \exp(-385/T)$	292–800	Pilgrim, McIlroy, and Taatjes, 1997[15]	PLP (h)
$(9.3 \pm 0.9) \times 10^{-14}$	292		
Reviews and Evaluations			
$1.1 \times 10^{-11} \exp(-1400/T)$	200–300	NASA, 1997[16]	(i)
$9.6 \times 10^{-12} \exp(-1350/T)$	200–300	IUPAC, 1997[17]	(j)

Comments

(a) These values were derived using the original data, but correcting for the presence of C_2H_6 (see Addenda to Watson, 1977[18]).

(b) Non-linear Arrhenius behavior was observed over the entire temperature range (200–500 K) of measurements. Data for the temperature range 200–299 K are well represented by the Arrhenius expression given in the table.[3]

(c) Non-linear Arrhenius behavior was observed over the entire temperature range (200–504 K) of measurements. Data for the temperature range 200–300 K are well represented by the Arrhenius expression given in the table.[6]

(d) Non-linear Arrhenius behavior was observed over the entire temperature range (220–423 K) of measurements. Data for the temperature range 220–298 K are well represented by the Arrhenius expression given in the table.[7]

(e) Non-linear Arrhenius behavior was observed. At temperatures at and below 240 K the apparent bimolecular rate constant was dependent upon the chemical composition of the reaction mixture. Ravishankara and Wine[8] suggested that this was due to a nonequilibration of the $^2P_{1/2}$ and $^2P_{3/2}$ spin states of atomic chlorine at high values of the pseudo-first order rate constant, k', i.e., if the mixture did not contain an efficient spin equilibrator, e.g., Ar or CCl_4, the bimolecular rate constant decreased at high CH_4 concentrations, i.e., high values of k'. The Arrhenius expression for k between 221 and 298 K was derived from the data shown in their Table II (excluding the high CH_4 concentration data in the $He-Cl_2-CH_4$ system).

(f) Very low pressure reactor system with MS detection of reactants and products.

(g) Turbulent flow tube technique at pressures near 80 mbar (60 Torr). The Cl atom decay was monitored by RF.

(h) Pulsed laser photolysis of CF_2Cl_2 at 193 nm. Time evolution of HCl product was monitored by continuous wave infrared long-path absorption at the R(3) line of the fundamental vibrational transition. Nonlinear Arrhenius behavior was observed between 292 and 800 K and was described by the modified Arrhenius expression given in the table.

(i) The 298 K rate coefficient was the average of the absolute rate coefficients reported by Watson *et al.*,[1] Manning and Kurylo,[2] Whytock *et al.*,[3] Michael and Lee,[4] Lin *et al.*,[5] Zahniser *et al.*,[6] Keyser,[7] and Ravishankara and Wine[8] and the relative rate coefficients of Pritchard *et al.*,[19,20] Knox,[21] Knox and Nelson,[22] and Lin *et al.*[5] The preferred Arrhenius expression was derived to best fit all of the reliable experimental data between 200 and 300 K.

(j) The preferred value at 298 K was obtained by taking the mean from the most reliable absolute (Watson *et al.*,[1] Manning and Kurylo,[2] Whytock *et al.*,[3] Michael and Lee,[4] Lin *et al.*,[5] Zahniser *et al.*,[6] Keyser,[7] and Ravishankara and Wine[8]) and the most reliable relative (Pritchard *et al.*,[19,20] Knox,[21] Knox and Nelson,[22] and Lin *et al.*[5]) rate coefficient studies. The preferred Arrhenius expression was derived to best fit all the reliable experimental data between 200 and 300 K.

Preferred Values

$k = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

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

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

Comments on Preferred Values

The preferred Arrhenius expression is derived from a least-squares fit to the experimental data between 200 and 300 K reported in the studies of Watson *et al.*,[1] Manning and Kurylo,[2] Whytock *et al.*,[3] Michael and Lee,[4] Lin *et al.*,[5] Zahniser*et al.*,[6] Keyser,[7] Ravishankara and Wine,[8] Heneghan *et al.*,[9] Dobis and Benson,[10] Sawerysyn *et al.*,[11] Beichert *et al.*,[12] Seeley *et al.*,[13] Matsumi *et al.*,[14] and Pilgrim *et al.*[15] The data used were restricted to the 200 300 K temperature range because of the curvature in the Arrhenius plot at higher temperatures reported in the studies of Whytock *et al.*,[3] Zahniser *et al.*,[6] Keyser,[7] Ravishankara and Wine,[8] and Pilgrim *et al.*[15] Therefore, for some studies only a subset of the data reported in the study was used. Results of relative rate studies were not used in this evaluation in the derivation of the preferred values. In general, the relative rate data (Refs. 5 and 18–21) used in previous evaluations are in good agreement with the preferred values at room temperature, but are significantly lower than the preferred values at low temperatures.

References

[1] R. T. Watson, G. Machado, S. Fischer, and D. D. Davis, J. Chem. Phys. **65**, 2126 (1976).

[2] R. G. Manning and M. J. Kurylo, J. Phys. Chem. **81**, 291 (1977).

[3] D. A. Whytock, J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, J. Chem. Phys. **66**, 2690 (1977).

[4] J. V. Michael and J. H. Lee, Chem. Phys. Lett. **51**, 303 (1977).

[5] C. L. Lin, M. T. Leu, and W. B. DeMore, J. Phys. Chem. **82**, 1772 (1978).

[6] M. S. Zahniser, B. M. Berquist, and F. Kaufman, Int. J. Chem. Kinet. **10**, 15 (1978).

[7] L. F. Keyser, J. Chem. Phys. **69**, 214 (1978).

[8] A. R. Ravishankara and P. H. Wine, J. Chem. Phys. **72**, 25 (1980).

[9] S. P. Heneghan, P. A. Knoot, and S. W. Benson, Int. J. Chem. Kinet. **13**, 677 (1981).

[10] O. Dobis and S. W. Benson, Int. J. Chem. Kinet. **19**, 691 (1987).

[11] J.-P. Sawerysyn, C. Lafage, B. Meriaux, and A. Tighezza, J. Chim. Phys. **84**, 1187 (1987).

[12] P. Beichert, L. Wingen, J. Lee, R. Vogt, M. J. Ezell, M. Ragains, R. Neavyn, and B. J. Finlayson-Pitts, J. Phys. Chem. **99**, 13156 (1995).

[13] J. V. Seeley, J. T. Jayne, and M. J. Molina, J. Phys. Chem. **100**, 4019 (1996).

[14] Y. Matsumi, K. Izumi, V. Skorokhodov, M. Kawasaki, and N. Tanaka, J. Phys. Chem. A **101**, 1216 (1997).

[15] J. S. Pilgrim, A. McIlroy, and C. A. Taatjes, J. Phys. Chem. A **101**, 1873 (1997).

[16] NASA Evaluation No. 12, 1997 (see references in Introduction).

[17] IUPAC, Supplement V, 1997 (see references in Introduction).

[18] R. T. Watson, J. Phys. Chem. Ref. Data **6**, 871 (1977).

[19] H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, J. Am. Chem. Soc. **76**, 1201 (1954).

[20] H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, J. Am. Chem. Soc. **77**, 2629 (1955).

[21] J. H. Knox, Chem. Indust. 1631 (1955); modified by Lin *et al.*[5]

[22] J. H. Knox and R. L. Nelson, Trans. Faraday Soc. **55**, 937 (1959).

$Cl + C_2H_2 + M \rightarrow C_2H_2Cl + M$

Low-pressure rate coefficients

Rate coefficient data

k_0 /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.15\pm0.30)\times10^{-21}\ T^{-3.5}$ [Ar]	210–361	Brunning and Stief, 1985[1]	FP-RF (a)
6.9×10^{-30} [Ar]	298		
Relative Rate Coefficients			
$(5.2\pm0.7)\times10^{-30}$ [air]	295	Wallington *et al.*, 1990[2]	(b)
$5.4\times10^{-30}\ (T/300)^{-2.092}$ [air]	252–370	Kaiser, 1992[3]	(c)
$(6.1\pm0.2)\times10^{-30}$ [air]	297	Kaiser and Wallington, 1996[4]	(d)
Reviews and Evaluations			
$5.9\times10^{-30}\ (T/300)^{-2.1}$ [air]	200–300	NASA, 1997[5]	(e)
$5.7\times10^{-30}\ (T/300)^{-3}$ [N_2]	200–300	IUPAC, 1997[6]	(f)

Comments

(a) The concentration of the bath gas Ar was varied over the range $(2.7-120)\times10^{17}$ molecule cm^{-3}. Some experiments with N_2 were also conducted. Falloff extrapolations were made using $F_c=0.6$.

(b) Cl atoms were generated by photolysis of Cl_2 in the presence of C_2H_2 and C_2H_6 (or C_2H_5Cl). The decays of C_2H_2, C_2H_6 (or C_2H_5Cl) were followed by FTIR spectroscopy. The measured rate coefficient ratios have been placed on an absolute basis using a rate coefficient of $k(Cl+C_2H_6)=5.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. Measurements were conducted over the pressure range 0.013 mbar–7.6 bar. Falloff extrapolations were made with $F_c=0.6$.

(c) Mixtures of C_2H_2, C_2H_6, Cl_2 and diluent (air, N_2, or SF_6) were irradiated by a UV fluorescent lamp. C_2H_2 and C_2H_6 concentrations were determined by GC. The reaction was studied at pressures between 0.03 and 1.7 bar. The measured rate coefficient ratios are placed on an absolute basis using the rate coefficient $8.68\times10^{-11}\exp(-113/T)$ cm^3 molecule^{-1} s^{-1} for the reaction $Cl+C_2H_6\rightarrow C_2H_5+HCl$. Falloff extrapolations were made with a temperature independent $F_c=0.6$.

(d) Mixtures of Cl_2, C_2H_2, CH_4, CH_3Cl, C_2H_6, and C_2H_5Cl and the diluent gases air and N_2 were irradiated with a UV fluorescent lamp. After irradiation C_2H_2, CH_4, and CH_3Cl were monitored by GC (0.4–13 mbar), CH_3Cl, C_2H_6, and C_2H_5Cl were determined by FTIR (13–920 mbar). The following values were used for the reference abstraction reactions: 1.0×10^{-13} cm^3 molecule^{-1} s^{-1} ($Cl+CH_4$), 4.9×10^{-13} cm^3 molecule^{-1} s^{-1} ($Cl+CH_3Cl$), 5.7×10^{-11} cm^3 molecule^{-1} s^{-1} ($Cl+C_2H_6$) and 8.05×10^{-12} cm^3 molecule^{-1} s^{-1} ($Cl+C_2H_5Cl$). The results were analyzed together with previous determinations performed between 0.13 and 7.9 bar and extrapolated with $F_c=0.6$.[2]

(e) Based on measurements of Refs. 3 and 4.

(f) Based on the preferred values of IUPAC, 1992[7] slightly modified to accommodate for the recent determination of Kaiser.[3]

Preferred Values

$k_0=6.1\times10^{-30}(T/300)^{-3}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0=\pm0.3$ at 298 K.
$\Delta n=\pm1$.

Comments on Preferred Values

The preferred values are based on the recent room temperature measurements of Kaiser and Wallington[4] which have been evaluated with $F_c=0.6$.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.52\pm0.15)\times10^{-4}\ T^{-2.63}$	210–361	Brunning and Stief, 1985[1]	FP-RF (a)
4.7×10^{-11}	298		
Relative Rate Coefficients			
$(2.3\pm0.7)\times10^{-10}$	295	Wallington *et al.*, 1990[2]	(b)
$2.13\times10^{-10}\ (T/300)^{-1.045}$	252–370	Kaiser, 1992[3]	(c)
$(2.0\pm0.1)\times10^{-10}$	297	Kaiser and Wallington, 1996[4]	(d)
Reviews and Evaluations			
$2.1\times10^{-10}\ (T/300)^{-1.0}$	200–300	NASA, 1997[5]	(e)
2.3×10^{-10}	200–300	IUPAC, 1997[6]	(f)

Comments

(a)–(f) See comment (a)–(f) for k_0.

Preferred Values

$k=5.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_\infty=2.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

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

$\Delta n=\pm1$.

Comments on Preferred Values

The preferred values are based on the data of Kaiser and Wallington[4] which cover the broadest pressure range (0.13–7.9 bar). They have been evaluated with $F_c=0.6$. With a choice of $F_c=0.4$, $k_0/[N_2]=7.1\times10^{-30}$ cm^3 molecule^{-1} s^{-1} and $k_\infty=3.5\times10^{-10}$ cm^3 molecule^{-1} s^{-1} would have been fitted at 298 K. Relative rate coefficients near 1 bar from Refs. 7–9 are in good agreement with the preferred values.

References

[1] J. Brunning and L. J. Stief, J. Chem. Phys. **83**, 1005 (1985).

[2] T. J. Wallington, J. M. Andino, I. M. Lorkovic, E. W. Kaiser, and G. Marston, J. Phys. Chem. **94**, 3644 (1990).

[3] E. W. Kaiser, Int. J. Chem. Kinet. **24**, 179 (1992).

[4] E. W. Kaiser and T. J. Wallington, J. Phys. Chem. **100**, 4111 (1996).

[5] NASA Evaluation No. 12, 1997 (see references in Introduction).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

[7] F. S. C. Lee and F. S. Rowland, J. Phys. Chem. **81**, 684 (1977).

[8] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

[9] T. J. Wallington, L. M. Skewes, and W. O. Siegl, J. Photochem. Photobiol. **A45**, 167 (1988).

$Cl + C_2H_4 + M \rightarrow C_2H_4Cl + M$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.6^{+1}_{-0.3})\times10^{-29}$ [air]	295	Wallington *et al.*, 1990[1]	RR (a)
$(1.7\pm0.3)\times10^{-29}\ (T/298)^{-3.28}$ [air]	297–383	Kaiser and Wallington, 1996[2]	(b)
$(1.42\pm0.05)\times10^{-29}$ [air]	297		
Reviews and Evaluations			
$1.6\times10^{-29}\ (T/300)^{-3.3}$ [air]	200–300	NASA, 1997[3]	(c)
$1.6\times10^{-29}\ (T/300)^{-3.5}$ [air]	200–300	IUPAC, 1997[4]	(d)

Comments

(a) Measurements of k performed by a relative rate technique. Cl atoms were generated by photolysis of Cl_2 in the presence of C_2H_4, and C_2H_6 (or C_2H_5Cl). Decay of C_2H_4, C_2H_6 (or C_2H_5Cl) monitored by FTIR spectroscopy. Using a value of 5.7×10^{-11} cm^3 molecule^{-1} s^{-1} for the rate coefficient for the $Cl+C_2H_6 \to C_2H_5 + HCl$ reaction, the relative data were placed on an absolute basis. The reaction was studied over the pressure range 13–4000 mbar and the measured rate coefficients fitted with $F_c = 0.6$.

(b) Mixtures of Cl_2, C_2H_4, CH_4, CH_3Cl, CCl_3H, C_2H_6, and C_2H_5Cl and the diluent gases air and N_2 were irradiated with a UV fluorescent lamp. After irradiation, C_2H_4 and the above reference compounds were determined by GC or FTIR techniques. The experiments were performed at total pressures of 0.26–130 mbar. The following values were used for the reference abstraction reactions: 1.0×10^{-13} cm^3 molecule^{-1} s^{-1} ($Cl+CH_4$), 4.9×10^{-13} cm^3 molecule^{-1} s^{-1} ($Cl+CH_3Cl$), 1.1×10^{-13} cm^3 molecule^{-1} s^{-1} ($Cl+CCl_3H$), 5.7×10^{-11} cm^3 molecule^{-1} s^{-1} ($Cl+C_2H_6$), and 8.05×10^{-12} cm^3 molecule^{-1} s^{-1} ($Cl+C_2H_5Cl$). The results were analyzed together with previous determinations conducted at 130–4000 mbar of air[1] and extrapolated with $F_c = 0.6$. The value $\Delta H^\circ_{f,298} = (295.4 \pm 1.7)$ kJ mol^{-1} for the C_2H_3 radical was derived from the measurements.

(c) Based on the data of Ref. 1. The temperature dependence is taken from Kaiser and Wallington.[2]

(d) Based on the measurements of Wallington *et al.*[1] and an estimated temperature dependence similar to that determined for the reaction $Cl+C_2H_2+M \to C_2H_2Cl+M$.

Preferred Values

$k_0 = 1.7\times10^{-29}(T/300)^{-3.3}[\text{air}]$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Values

The new measurements of Ref. 2 together with previous determinations[1] allow for an extrapolation to k_0 ($F_c = 0.6$ was used). The temperature dependence is from Ref. 2.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(3.05^{+2}_{-0.4})\times10^{-10}$	295	Wallington *et al.*, 1990[1]	FP-FTIR (a)
$(3.2\pm0.15)\times10^{-10}$	297	Kaiser and Wallington, 1996[2]	(b)
Reviews and Evaluations			
$3.1\times10^{-10}\,(T/300)^{-1.0}$	200–300	NASA, 1997[3]	(c)
3×10^{-10}	250–300	IUPAC, 1997[4]	(d)

Comments

(a)–(d) See comments (a)–(d) for k_0.

Preferred Values

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

$k_\infty = 3\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–300 K.

Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Values

The falloff extrapolation of the data from Ref. 1 with $F_c = 0.6$ is consistent with results in the intermediate falloff range.[5–9] The new results of Kaiser and Wallington[2] are in very good agreement with their previous results.[1]

References

[1] T. J. Wallington, J. M. Andino, I. M. Lorkovic, E. W. Kaiser, and G. Marston, J. Phys. Chem. **94**, 3644 (1990).

[2] E. W. Kaiser and T. J. Wallington, J. Phys. Chem. **100**, 4111 (1996).

[3] NASA Evaluation No. 12, 1997 (see references in Introduction).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

[5] F. S. C. Lee and F. S. Rowland, J. Phys. Chem. **81**, 1235 (1977).

[6] S. R. Iyer, P. J. Rogers, and F. S. Rowland, J. Phys. Chem. **87**, 3799 (1983).

[7] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

[8] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **19**, 1097 (1987).

[9] T. J. Wallington, L. M. Skewes, and W. O. Siegl, J. Photochem. Photobiol. **A45**, 167 (1988).

$Cl + C_2H_6 \rightarrow HCl + C_2H_5$

$\Delta H° = -8.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comment
Absolute Rate Coefficients			
$(6.0\pm1.5)\times10^{-11}$	298	Davis, Braun, and Bass, 1970[1]	FP-RF (a)
7.29×10^{-11} exp$[-(61\pm44)/T]$	222–322	Manning and Kurylo, 1977[2]	FP-RF
$(5.93\pm0.44)\times10^{-11}$	296		
$(5.95\pm0.28)\times10^{-11}$	298	Ray, Keyser, and Watson, 1980[3]	DF-MS
9.01×10^{-11} exp$[-(133\pm15)/T]$	220–604	Lewis *et al.*, 1980[4]	DF-RF
$(5.48\pm0.30)\times10^{-11}$	298		
8.20×10^{-11} exp$[-(86\pm10)/T]$	203–343	Dobis and Benson, 1991[5]	(b)
$(6.10\pm0.11)\times10^{-11}$	298		
$(7.05\pm1.4)\times10^{-11}$	298	Kaiser *et al.*, 1992[6]	PLP-IRA
$(5.9\pm0.6)\times10^{-11}$	297	Stickel *et al.*, 1992[7]	PLP-TDLS
$(5.53\pm0.21)\times10^{-11}$	298	Beichert *et al.*, 1995[8]	DF-RF
$(5.75\pm0.45)\times10^{-11}$	298	Tyndall *et al.*, 1997[9]	FP-RF
8.6×10^{-11} exp$[-(135\pm26)]$	292–600	Pilgrim *et al.*, 1997[10]	PLP (c)
$(5.5\pm0.2)\times10^{-11}$	292		
Relative Rate Coefficients			
$(6.5\pm1.3)\times10^{-11}$	296	Hooshiyar and Niki, 1995[11]	RR (d)
$(5.7\pm1.2)\times10^{-11}$	298	Beichert *et al.*, 1995[8]	RR (e)
$(5.9\pm1.2)\times10^{-11}$	297	Tyndall *et al.*, 1997[9]	RR (f)
Reviews and Evaluations			
7.7×10^{-11} exp$(-90/T)$	220–350	NASA, 1997[12]	(g)
8.1×10^{-11} exp$(-95/T)$	220–600	IUPAC, 1997[13]	(h)

Comments

(a) Reported value has been reduced by 10% as discussed previously.[14]

(b) Very low pressure reactor study. Cl atoms were generated by microwave discharge of Cl_2–He mixtures, with MS analysis of reactants and products.

(c) Cl atoms generated from pulsed laser photolysis of CF_2Cl_2 at 193 nm. Time evolution of HCl product was monitored by continuous wave infrared long-path absorption at the R(3) line of the fundamental vibrational transition.

(d) Cl atoms generated by photolysis of Cl_2 in N_2 at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(Cl+n\text{-}C_4H_{10}) = 0.294\pm0.023$ is placed on an absolute basis by use of $k(Cl+n\text{-}C_4H_{10}) = 2.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) Cl atoms generated by photolysis of Cl_2 in air at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(Cl+n\text{-}C_4H_{10}) = 0.261\pm0.013$ is placed on absolute basis by use of $k(Cl+n\text{-}C_4H_{10}) = 2.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(f) Cl atoms generated by photolysis of Cl_2 in air or N_2 at a total pressure of 156–666 mbar (117–500 Torr). Relative disappearance rates of organics studied were measured by GC or FTIR. Rate coefficient ratio $k/k(Cl+n\text{-}C_4H_{10}) = 0.267\pm0.037$ is placed on absolute basis by use of $k(Cl+n\text{-}C_4H_{10}) = 2.2\times10^{-1}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(g) The 298 K rate coefficient was the mean of the absolute rate coefficients of Davis *et al.*,[1] Manning an Kurylo,[2] Ray *et al.*,[3] and Lewis *et al.*,[4] with the temperature dependence being that which best fit the dat of Manning and Kurylo[2] and Lewis *et al.*[4] The result of Dobis and Benson,[5] Kaiser *et al.*,[6] Beichert *et al.*, and Hooshiyar and Niki[11] were in good agreement wit the recommendation.

(h) The 298 K rate coefficient was the average of the roo temperature rate coefficients of Davis *et al.*,[1] Mannin and Kurylo,[2] Ray *et al.*,[3] Lewis *et al.*,[4] Dobis an Benson,[5] and Stickel *et al.*[7] The temperature dependence was the average of those from the studies o Manning and Kurylo,[2] Lewis *et al.*,[4] and Dobis an Benson.[5]

Preferred Values

$k = 5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.3\times10^{-11}$ exp$(-100/T)$ cm^3 molecule^{-1} s^{-1} over th temperature range 220–600 K.

Reliability

$\Delta \log k = \pm0.06$ at 298 K.

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

Comments on Preferred Values

The 298 K rate coefficient is the average of the room temperature absolute rate coefficients of Davis *et al.*,[1] Manning and Kurylo,[2] Ray *et al.*,[3] Lewis *et al.*,[4] Dobis and Benson,[5] Kaiser *et al.*,[6] Stickel *et al.*,[7] Beichert *et al.*,[8] Tyndall *et al.*,[9] and Pilgrim *et al.*[10] The temperature dependence is the average of those from the temperature-dependent studies of Manning and Kurylo,[2] Lewis *et al.*,[4] Dobis and Benson,[5] and Pilgrim *et al.*[10] The room temperature relative rate values of Hooshiyar and Niki,[11] Beichert *et al.*,[8] and Tyndall *et al.*[9] are in good agreement with the preferred value, while those of Atkinson and Aschmann[15] and Wallington *et al.*[16] are 20%–30% higher than the preferred value.

References

[1] D. D. Davis, W. Braun, and A. M. Bass, Int. J. Chem. Kinet. **2**, 101 (1970).
[2] R. G. Manning and M. J. Kurylo, J. Phys. Chem. **81**, 291 (1977).
[3] G. W. Ray, L. F. Keyser, and R. T. Watson, J. Phys. Chem. **84**, 1674 (1980).
[4] R. S. Lewis, S. P. Sander, S. Wagner, and R. T. Watson, J. Phys. Chem. **84**, 2009 (1980).
[5] O. Dobis and S. W. Benson, J. Am. Chem. Soc. **113**, 6377 (1991).
[6] E. W. Kaiser, L. Rimai, E. Schwab, and E. C. Lim, J. Phys. Chem. **96**, 303 (1992).
[7] R. E. Stickel, J. M. Nicovich, S. Wang, Z. Zhao, and P. H. Wine, J. Phys. Chem. **96**, 9875 (1992).
[8] P. Beichert, L. Wingen, J. Lee, R. Vogt, M. J. Ezell, M. Ragains, R. Neavyn, and B. J. Finlayson-Pitts, J. Phys. Chem. **99**, 13156 (1995).
[9] G. S. Tyndall, J. J. Orlando, T. J. Wallington, M. Dill, and E. W. Kaiser, Int. J. Chem. Kinet. **29**, 43 (1997).
[10] J. S. Pilgrim, A. McIlroy, and C. A. Taatjes, J. Phys. Chem. A **101**, 1873 (1997).
[11] P. A. Hooshiyar and H. Niki, Int. J. Chem. Kinet. **27**, 1197 (1995).
[12] NASA Evaluation No. 12, 1997 (see references in Introduction).
[13] IUPAC, Supplement V, 1997 (see references in Introduction).
[14] CODATA, 1980 (see references in Introduction).
[15] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).
[16] T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).

$Cl + C_3H_6 + M \rightarrow C_3H_6Cl + M$

Low-pressure rate coefficients

Rate coefficient data

k_0 /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(4.0\pm0.4)\times10^{-28}$ [N_2]	298	Kaiser and Wallington, 1996[1]	(a)

Comments

(a) Cl atoms were generated by photolysis of Cl_2 in the presence of C_3H_6, C_2H_6, and 1–900 mbar of N_2. C_3H_6 consumption was determined by FTIR or GC analysis, the major products being 3-chloropropene and 1,2-dichloropropane. At low pressure (below 12 mbar) 3-chloropropene is the major product indicating that the abstraction of H by Cl from the C_3H_6 is the dominant channel. At pressures higher than 12 mbar, the primary product observed is 1,2-dichloropropane, indicating that addition of a Cl atom to the double bond is the major channel. The limiting rate coefficients were obtained using $F_c=0.6$. A rate coefficient for the reference reaction $Cl+C_2H_6\rightarrow C_2H_5+HCl$ of 5.9×10^{-11} cm^3 molecule^{-1} s^{-1} was employed.[1]

Preferred Values

$k_0=4.0\times10^{-28}$ [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is based on the only value reported.[1] Due to this and to the uncertainty of the extrapolated k_0, a large error limit is assigned.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comment:
Relative Rate Coefficients			
$(2.44 \pm 0.08) \times 10^{-10}$	296	Atkinson and Aschmann, 1985[2]	(a)
$(3.22 \pm 0.13) \times 10^{-10}$	295	Wallington, Skewes, and Siegl, 1983[3]	(b)
$(2.7 \pm 0.4) \times 10^{-10}$	298	Kaiser and Wallington, 1996[1]	(c)

Comments

(a) Cl atoms generated by the photolysis of Cl_2-n-C_4H_{10}–C_3H_6–air mixtures at 1 bar. The reaction was studied relative to the reaction $Cl + n\text{-}C_4H_{10} \rightarrow$ products for which a rate coefficient 1.97×10^{-10} cm^3 molecule^{-1} s^{-1} was used. C_3H_6 and n-C_4H_{10} were analyzed by GC.

(b) Cl atoms were formed by photolysis of Cl_2 in the presence of C_3H_6 and C_2H_6 or n-C_4H_{10} at atmospheric pressure of synthetic air. The decay rate of C_3H_6 was measured relative to that of C_2H_6 or n-C_4H_{10} and placed on an absolute basis using rate coefficients of 5.7×10^{-11} cm^3 molecule^{-1} s^{-1} and 2.25×10^{-10} cm^3 molecule^{-1} s^{-1} for the reference reactions, respectively.

(c) See comment (a) for k_0.

Preferred Values

$k = 2.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_\infty = 2.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is an average of earlier results fron Refs. 2 and 3 and the more recent determination by Kaise and Wallington.[1] At room temperature and atmospheric pres sure, the addition of Cl atoms to the double bond account for approximately 90% of the reaction.[1] The H atom abstrac tion occurs from the C–H bonds of the methyl group.[1]

References

[1] E. W. Kaiser and T. J. Wallington, J. Phys. Chem. **100**, 9788 (1996).

[2] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

[3] T. J. Wallington, L. M. Skewes, and W. O. Siegl, J. Photochem. Photo biol. A: Chem. **45**, 167 (1988).

$Cl + C_3H_8 \rightarrow HCl + n\text{-}C_3H_7$ (1)

$\rightarrow HCl + i\text{-}C_3H_7$ (2)

$\Delta H°(1) = -11.6$ kJ·mol^{-1}
$\Delta H°(2) = -19.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.36×10^{-10} exp[$(44\pm25)/T$]	220–607	Lewis *et al.*, 1980[1]	DF-RF (a)
$(1.51\pm0.06)\times10^{-10}$	298		
$(1.23\pm0.10)\times10^{-10}$	298	Beichert *et al.*, 1995[2]	DF-RF (b)
$(1.38\pm0.03)\times10^{-10}$	292–700	Pilgrim, McIlroy, and Taatjes, 1997[3]	PLP (c)
Relative Rate Coefficients			
$(1.50\pm0.30)\times10^{-10}$	296	Atkinson and Aschmann, 1985[4]	RR (d)
$(1.56\pm0.30)\times10^{-10}$	295	Wallington *et al.*, 1988[5]	RR (e)
$(1.44\pm0.30)\times10^{-10}$	296	Hooshiyar and Niki, 1995[6]	RR (f)
$(1.44\pm0.26)\times10^{-10}$	298	Beichert *et al.*, 1995[2]	RR (g)
$(1.43\pm0.25)\times10^{-10}$	297	Tyndall *et al.*, 1997[7]	RR (h)
Reviews and Evaluations			
1.2×10^{-10} exp$(40/T)$	220–600	NASA, 1997[8]	(i)
1.2×10^{-10} exp$(40/T)$	220–600	IUPAC, 1997[9]	(j)

Comments

(a) Rate constant was measured at three temperatures: 220, 298, and 607 K. Within experimental uncertainty, these three values were the same. Authors gave as an alternative rate expression the simple mean of the three values: $k = (1.58\pm0.13)\times10^{-10}$ cm^3 molecule^{-1} s^{-1}.

(b) Both relative and absolute rate studies of reactions of Cl atoms with C_1–C_4 alkanes. Direct measurement of ratio $k/k(Cl+C_2H_6)$ is in good agreement with the ratio of the absolute values.

(c) Cl atoms were generated from pulsed laser photolysis of CF_2Cl_2 at 193 nm. Time evolution of HCl product was monitored by continuous wave infrared long-path absorption at the R(3) line of the fundamental vibrational transition.

(d) Cl atoms were generated by photolysis of Cl_2 in air at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(Cl+n\text{-}C_4H_{10}) = 0.681\pm0.025$ is placed on absolute basis by use of $k(Cl+n\text{-}C_4H_{10}) = 2.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) Cl atoms were generated by photolysis of Cl_2 in air at 990 mbar (740 Torr) pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(Cl+n\text{-}C_4H_{10}) = 0.711\pm0.019$ is placed on absolute basis by use of $k(Cl+n\text{-}C_4H_{10}) = 2.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(f) Cl atoms were generated by photolysis of Cl_2 in N_2 at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(Cl+n\text{-}C_4H_{10}) = 0.656\pm0.009$ is placed on absolute basis by use of $k(Cl+n\text{-}C_4H_{10}) = 2.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(g) Cl atoms were generated by photolysis of Cl_2 in air at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(Cl+C_2H_6) = 2.44\pm0.26$ is placed on absolute basis by use of $k(Cl+C_2H_6) = 5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(h) Cl atoms were generated by photolysis of Cl_2 in air or N_2 at a total pressure of 156–666 mbar (117–500 Torr). Relative disappearance rates of organics studied were measured by GC or FTIR. Rate coefficient ratio $k/k(Cl+C_2H_6) = 2.42\pm0.10$ is placed on absolute basis by use of $k(Cl+C_2H_6) = 5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(i) Based on results of absolute rate studies of Lewis *et al.*[1] and Beichert *et al.*,[2] and the relative rate studies of Atkinson and Aschmann,[4] Wallington *et al.*,[5] Hooshiyar and Niki,[6] Pritchard *et al.*,[10] and Knox and Nelson.[11]

(j) Based on results of the absolute rate study of Lewis *et al.*,[1] and the relative rate studies of Atkinson and Aschmann,[4] Wallington *et al.*,[5] Pritchard *et al.*,[10] and Knox and Nelson.[11]

Preferred Values

$k = 1.4\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–700 K.

Reliability

Δ log $k = \pm 0.06$ at 298 K.
Δ$(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred value at room temperature is the mean of the absolute values reported by Lewis *et al.*,[1] Beichert *et al.*,[2] and Pilgrim *et al.*,[3] and the relative values reported by Atkinson and Aschmann,[4] Wallington *et al.*,[5] Hooshiyar and Niki,[6] Beichert *et al.*,[2] and Tyndall *et al.*[7] The temperature independence is based on the results of Lewis *et al.*[1] over the range 220–607 K and those of Pilgrim *et al.*[3] over the range 292–700 K. Tyndall *et al.*[7] studied the mechanism of the reaction at 298 K and reported the yield of 1-propyl radicals to be (43±3)% and that of 2-propyl radicals to be (57 ±3)%.

References

[1] R. S. Lewis, S. P. Sander, S. Wagner, and R. T. Watson, J. Phys. Chem. **84**, 2009 (1980).
[2] P. Beichert, L. Wingen, J. Lee, R. Vogt, M. J. Ezell, M. Ragains, R. Neavyn, and B. J. Finlayson-Pitts, J. Phys. Chem. **99**, 13156 (1995).
[3] J. S. Pilgrim, A. McIlroy, and C. A. Taatjes, J. Phys. Chem. A **101**, 1873 (1997).
[4] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).
[5] T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).
[6] P. A. Hooshiyar and H. Niki, Int. J. Chem. Kinet. **27**, 1197 (1995).
[7] G. S. Tyndall, J. J. Orlando, T. J. Wallington, M. Dill, and E. W. Kaiser, Int. J. Chem. Kinet. **29**, 43 (1997).
[8] NASA Evaluation No. 12, 1997 (see references in Introduction).
[9] IUPAC, Supplement V, 1997 (see references in Introduction).
[10] H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, J. Am. Chem. Soc. **77**, 2629 (1955).
[11] J. H. Knox and R. L. Nelson, Trans. Faraday Soc. **55**, 937 (1959).

$Cl + n\text{-}C_4H_{10} \rightarrow HCl + C_4H_9$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.15\times10^{-10}\exp[(12\pm26)/T]$	298–598	Lewis *et al.*, 1980[1]	DF-RF (a)
$(2.25\pm0.10)\times10^{-10}$	298		
$(1.8\pm0.2)\times10^{-10}$	298	Nesbitt and Leone, 1982[2]	(b)
$(2.11\pm0.18)\times10^{-10}$	298	Beichert *et al.*, 1995[3]	DF-RF (c)
$(2.15\pm0.15)\times10^{-10}$	298	Tyndall *et al.*, 1997[4]	FP-RF (d)

Comments

(a) Rate constant was measured at three temperatures: 298, 422, and 598 K. Within experimental uncertainty, these three values were the same. Authors gave as an alternative rate expression the simple mean of the three values: $k = (2.20\pm0.10)\times10^{-10}$ cm^3 molecule^{-1} s^{-1}.

(b) Laser photodissociation of Cl_2 with time-resolved monitoring of infrared emission of HCl ($v=1$) product.

(c) Both relative and absolute rate studies of reactions of Cl atoms with C_1–C_4 alkanes. Direct measurement of ratio $k/k(Cl+C_2H_6)$ is in very good agreement with the ratio of the absolute values.

(d) Both relative and absolute rate studies of reactions of Cl atoms with C_2H_6, C_3H_8, and n-C_4H_{10}. Measurements of $k/k(Cl+C_2H_6)$ over the temperature range 298–540 K support the essentially zero temperature dependence for k reported by Lewis *et al.*[1] GC measurements at 298 K show that the reaction $Cl+n\text{-}C_4H_{10}$ yields (29±2)% 1-butyl radicals and (71±2)% 2-butyl radicals.

Preferred Values

$k = 2.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–600 K.

Reliability

Δ log $k = \pm 0.06$ at 298 K.
Δ$(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred value at room temperature is the mean of the values reported by Lewis *et al.*,[1] Beichert *et al.*,[3] and Tyndall *et al.*[4] The temperature independence is based on the results of Lewis *et al.*[1] over the range 298–598 K and is supported by the relative measurements of Tyndall *et al.*[4] over the range 298–540 K. Tyndall *et al.*[4] studied the mechanism of the reaction at 298 K and reported the yield of 1-butyl radicals to be (29±2)% and that of 2-butyl radicals to be (71±2)%.

References

[1] R. S. Lewis, S. P. Sander, S. Wagner, and R. T. Watson, J. Phys. Chem. **84**, 2009 (1980).
[2] D. J. Nesbitt and S. R. Leone, J. Phys. Chem. **86**, 4962 (1982).
[3] P. Beichert, L. Wingen, J. Lee, R. Vogt, M. J. Ezell, M. Ragains, R. Neavyn, and B. J. Finlayson-Pitts, J. Phys. Chem. **99**, 13156 (1995).
[4] G. S. Tyndall, J. J. Orlando, T. J. Wallington, M. Dill, and E. W. Kaiser, Int. J. Chem. Kinet. **29**, 43 (1997).

$Cl + HCHO \rightarrow HCl + HCO$

$\Delta H^\circ = -61.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.48 \pm 0.50) \times 10^{-11}$	200–500	Michael *et al.*, 1979[1]	FP-RF
$1.09 \times 10^{-10} \exp[-(131 \pm 98)/T]$	223–323	Anderson and Kurylo, 1979[2]	FP-RF
$(7.18 \pm 0.61) \times 10^{-11}$	293		
$(7.4 \pm 0.7) \times 10^{-11}$	298	Fasano and Nogar, 1981[3]	PLP-CL
Relative Rate Coefficients			
$(7.6 \pm 0.6) \times 10^{-11}$	298	Niki *et al.*, 1978[4]	RR (a)
$(6.8 \pm 1.4) \times 10^{-11}$	295	Poulet, Laverdet, and Le Bras, 1981[5]	RR (b)
Reviews and Evaluations			
$8.1 \times 10^{-11} \exp(-30/T)$	200–500	NASA, 1997[6]	(c)
$8.2 \times 10^{-11} \exp(-34/T)$	200–500	IUPAC, 1997[7]	(d)

Comments

(a) Competitive photochlorination between HCHO and C_2H_6 using FTIR. The measured rate coefficient ratio $k/k(Cl+C_2H_6) = 1.3 \pm 0.1$ is placed on an absolute basis by use of $k(Cl+C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) DF-MS study. Value of k derived from measured ratio of $k/k(Cl+C_2H_6) = 1.16 \pm 0.12$ and $k(Cl+C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Based on data in Refs. 1–5.

(d) See Comments on Preferred Values.

Preferred Values

$k = 7.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.2 \times 10^{-11} \exp(-34/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–500 K.

Reliability

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

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

Comments on Preferred Values

The preferred temperature dependence is based on a least-squares fit to the 200–500 K data of Michael *et al.*[1] and the 223–323 K data of Anderson and Kurylo.[2] The preferred 298 K rate coefficient is based on these absolute studies[1,2] and the room temperature data of Niki *et al.*,[4] Fasano and Nogar,[3] and Poulet *et al.*,[5] all of which are in good agreement. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[7]

References

[1] J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, J. Chem. Phys. **70**, 1147 (1979).

[2] P. C. Anderson and M. J. Kurylo, J. Phys. Chem. **83**, 2053 (1979).

[3] D. M. Fasano and N. S. Nogar, Int. J. Chem. Kinet. **13**, 325 (1981).

[4] H. Niki, P. D. Maker, L. P. Breitenbach, and C. M. Savage, Chem. Phys. Lett. **57**, 596 (1978).

[5] G. Poulet, G. Laverdet, and G. Le Bras, J. Phys. Chem. **85**, 1892 (1981).

[6] NASA Evaluation No. 12, 1997 (see references in Introduction).

[7] IUPAC, Supplement V, 1997 (see references in Introduction).

$$Cl + CH_3CHO \rightarrow HCl + CH_3CO \qquad (1)$$

$$\rightarrow HCl + CH_2CHO \qquad (2)$$

$\Delta H°(1) = -57.8\ kJ \cdot mol^{-1}$
$\Delta H°(2) = -37.3\ kJ \cdot mol^{-1}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Commen
Absolute Rate Coefficients			
$(6.6 \pm 1.4) \times 10^{-11}$	210–343	Payne *et al.*, 1990[1]	FP-RF
Relative Rate Coefficients			
$(7.9 \pm 1.2) \times 10^{-11}$	298	Niki *et al.*, 1985[2]	RR (a)
$(8.15 \pm 0.82) \times 10^{-11}$	295 ± 2	Wallington *et al.*, 1988[3]	RR (b)
$(6.14 \pm 0.54) \times 10^{-11}$	298	Bartels, Hoyermann, and Lange, 1989[4]	RR (c)
Branching Ratios			
$k_2/k < 0.01$	298	Niki *et al.*, 1985[2]	(a)
$k_2/k < 0.07$	298	Bartels, Hoyermann, and Lange, 1989[4]	(c)
Reviews and Evaluations			
7.2×10^{-11}	210–340	IUPAC, 1997[5]	(d)

Comments

(a) Cl atoms were generated by photolysis of Cl_2 at 930 mbar (700 Torr) total pressure of N_2. Relative decay rates of CH_3CHO and C_2H_6 measured, and the measured rate coefficient ratio is placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation). The branching ratio was determined from FTIR spectroscopic product analysis.

(b) Cl atoms were generated from the photolysis of Cl_2 in Cl_2–N_2–CH_3CHO–C_2H_6 mixtures and the relative decay rates of CH_3CHO and C_2H_6 measured. The measured rate coefficient ratio is placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) DF-MS study. Relative decay rates of CH_3CHO and C_2H_6 were monitored, and the measured rate coefficient ratio is placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation). The branching ratio was derived from the products observed by MS.

(d) See Comments on Preferred Values.

Preferred Values

$k = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 210–340 K.

$k_2/k < 0.05$ at 298 K.

Reliability

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

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

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of tł absolute rate coefficient of Payne *et al.*[1] and the relative raı coefficients of Niki *et al.*,[2] Wallington *et al.*,[3] and Barte *et al.*[4] The lack of a temperature dependence of the rate cc efficient is consistent with the data of Payne *et al.*[1] Th branching ratio is derived from the data of Niki *et al.*[2] an Bartels *et al.*[4] The relative rate coefficient of Scollard *et al* is ~30% higher than the preferred values, which are ident cal to those in our previous evaluation, IUPAC, 1997.[5]

References

[1] W. A. Payne, D. F. Nava, F. L. Nesbitt, and L. J. Stief, J. Phys. Chem. 9 7190 (1990).

[2] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phy Chem. **89**, 588 (1985).

[3] T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japa Int. J. Chem. Kinet. **20**, 867 (1988).

[4] M. Bartels, K. Hoyermann, and U. Lange, Ber. Bunsenges. Phys. Chen **93**, 423 (1989).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

[6] D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, (Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, J. Phys. Chem. 9' 4683 (1993).

$Cl + C_2H_5CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.17\pm0.10)\times10^{-10}$	295 ± 2	Wallington *et al.*, 1988[1]	RR (a)
Reviews and Evaluations			
1.2×10^{-10}	298	IUPAC, 1997[2]	(b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2–air mixtures, and the decay rates of C_2H_5CHO and C_2H_6 monitored by GC. The measured rate coefficient ratio is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) See Comments on Preferred Values.

Preferred Values

$k=1.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

Based on the sole study of Wallington *et al.*,[1] with expanded uncertainty limits, and is identical to that in our previous evaluation, IUPAC, 1997.[2]

References

[1] T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$Cl + CH_3COCH_3 \rightarrow HCl + CH_3COCH_2$

$\Delta H° = -20.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(3.5\pm0.5)\times10^{-12}$	295 ± 2	Wallington *et al.*, 1990[1]	RR (a)
$(1.7\pm0.3)\times10^{-12}$	294 ± 1	Olsson *et al.*, 1997[2]	RR (b)
Reviews and Evaluations			
3.5×10^{-12}	298	IUPAC, 1997[3]	(c)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2–air (or N_2)–CH_3COCH_3–C_2H_5Cl mixtures. From the relative decays of CH_3COCH_3 and C_2H_5Cl, a rate coefficient ratio of $k(Cl+CH_3COCH_3)k(Cl+C_2H_5Cl)=0.295\pm0.015$ was obtained. Combined with a measurement of $k(Cl+C_2H_5Cl)/k(Cl+C_2H_6)=0.201\pm0.027$[1] and $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation), the value cited in the table is obtained.

(b) Cl atoms were generated by pulsed laser photolysis of Cl_2 at 355 nm followed by competition between the reactions $Cl+CH_3COCH_3$ and $Cl+ClONO_2 \rightarrow Cl_2+NO_3$. The formation of NO_3 with and without acetone in the reaction mixture was monitored by TDLS at 661.8 nm. The value recommended in Yokelson *et al.*[4] for the value of the rate constant of the reference reaction ($Cl+ClONO_2$) was used.

(c) Based on results of the relative rate study of Wallington *et al.*[1]

Preferred Values

$k=3.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K

Reliability

Δ log $k=\pm 0.3$ at 298 K.

Comments on Preferred Values

Because of the potential for errors in the experimental technique of Olsson *et al.*[2] (the assumption that Cl atoms only react with $ClONO_2$ and acetone, the need for absolute concentration measurements of acetone, and the experimental approach of sequential experiments in the presence and absence of acetone), the preferred 298 K rate coefficient is based on the rate coefficient obtained from the relative rate study of Wallington *et al.*[1]

References

[1] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

[2] B. E. R. Olsson, M. Hallquist, E. Ljungström, and J. Davidson, Int. J. Chem. Kinet. **29**, 195 (1997).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

[4] R. J. Yokelson, J. B. Burkholder, L. Goldfarb, R. W. Fox, M. K. Gilles, and A. R. Ravishankara, J. Phys. Chem. **99**, 13976 (1995).

$Cl + CH_3COCH_2CH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.28\pm 0.59)\times 10^{-11}$	295	Wallington *et al.*, 1990[1]	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2–N_2–$CH_3COC_2H_5$–C_2H_6 mixtures at 930 mbar (700 Torr) total pressure, and the $CH_3COC_2H_5$ and C_2H_6 concentrations monitored by FTIR absorption spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of $k(Cl+C_2H_6) = 5.9\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k=4.3\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

Δ log $k=\pm 0.2$ at 298 K.

Comments on Preferred Values

Based on the sole reported study of Wallington *et al.*,[1] with expanded uncertainty limits. This result is supported by the value of $k=(3.8\pm 0.3)\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} quoted in Niki *et al.*[2] as unpublished results from that laboratory.

References

[1] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

[2] H. Niki, P. D. Maker, C. M. Savage, L. P. Breitenbach, and M. D. Hurley, J. Phys. Chem. **91**, 941 (1987).

$Cl + CH_3OH \rightarrow HCl + CH_2OH$

$\Delta H° = -29.8\ kJ \cdot mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.33 \pm 0.70) \times 10^{-11}$	200-500	Michael *et al.*, 1979[1]	FP-RF
$(6.14 \pm 0.67) \times 10^{-11}$	298 ± 2	Dóbé *et al.*, 1993[2]	DF-EPR
Relative Rate Coefficients			
$(4.73 \pm 0.42) \times 10^{-11}$	295 ± 2	Wallington *et al.*, 1988[3]	RR (a)
$(4.79 \pm 0.36) \times 10^{-11}$	298 ± 2	Nelson *et al.*, 1990[4]	RR (b)
$(5.3 \pm 1.2) \times 10^{-11}$	248-573	Lightfoot *et al.*, 1990[5]	RR (c)
Reviews and Evaluations			
5.4×10^{-11}	200-500	NASA, 1997[6]	(d)
5.5×10^{-11}	200-580	IUPAC, 1997[7]	(e)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2–CH_3OH–C_2H_6–air (N_2) mixtures at 1 bar total pressure. Concentrations of CH_3OH and C_2H_6 were monitored by GC and a rate coefficient ratio $k(Cl+CH_3OH)/k(Cl+C_2H_6) = 0.802 \pm 0.071$ determined. This rate coefficient ratio is placed on an absolute basis by use of $k(Cl+C_2H_6) = 5.9 \times 10^{-11}\ cm^3$ $molecule^{-1}\ s^{-1}$ (this evaluation).

(b) Cl atoms were generated from the photolysis of Cl_2 or $COCl_2$ in Cl_2 (or $COCl_2$)–N_2 (or O_2)–CH_3OH–cyclohexane mixtures at 1 bar pressure. Concentrations of CH_3OH and cyclohexane were measured by GC, and the rate coefficient ratio is placed on an absolute basis by use of $k(Cl+cyclohexane) = 3.11 \times 10^{-10}$ $cm^3\ molecule^{-1}\ s^{-1}$.[8]

(c) Derived from the measured initial HO_2 and CH_3O_2 radical concentrations in flash photolyzed Cl_2–CH_3OH–CH_4–N_2–O_2 mixtures, with the HO_2 and CH_3O_2 concentrations being measured by time-resolved UV absorption. Placed on an absolute basis by use of $k(Cl+CH_4) = 9.6 \times 10^{-12} \exp(-1350/T)\ cm^3$ $molecule^{-1}\ s^{-1}$.

(d) Based on the absolute rate coefficients of Michael *et al.*[1] and Dóbé *et al.*,[2] and the relative rate coefficients of Wallington *et al.*,[3] Nelson *et al.*,[4] and Lightfoot *et al.*[5]

(e) See Comments on Preferred Values.

Preferred Values

$k = 5.5 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$, independent of temperature over the range 200–580 K.

Reliability

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

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

Comments on Preferred Values

The preferred 298 K value is the average of the rate coefficients of Michael *et al.*,[1] Wallington *et al.*,[3] Nelson *et al.*,[4] Lightfoot *et al.*,[5] and Dóbé *et al.*,[2] and is in excellent agreement with the absolute rate coefficient of $(5.1 \pm 1.0) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K determined by Payne *et al.*[9] for the reaction $Cl+CH_3OD \rightarrow HCl+CH_2OD$. The zero temperature dependence is taken from the studies of Michael *et al.*[1] and Lightfoot *et al.*[5] It has been established that the reaction proceeds by H-atom abstraction from the methyl group rather than from the hydroxyl group (see Radford *et al.*,[10] Payne *et al.*,[9] Meier *et al.*,[11] and Dóbé *et al.*[12]). The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[7]

References

[1] J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, J. Chem. Phys. **70**, 3652 (1979).

[2] S. Dóbé, M. Otting, F. Temps, H. Gg. Wagner, and H. Ziemer, Ber. Bunsenges Phys. Chem. **97**, 877 (1993).

[3] T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).

[4] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

[5] P. D. Lightfoot, B. Veyret, and R. Lesclaux, J. Phys. Chem. **94**, 708 (1990).

[6] NASA Evaluation No. 12, 1997 (see references in Introduction).

[7] IUPAC, Supplement V, 1997 (see references in Introduction).

[8] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

[9] W. A. Payne, J. Brunning, M. B. Mitchell, and L. J. Stief, Int. J. Chem. Kinet. **20**, 63 (1988).

[10] H. E. Radford, K. M. Evenson, and D. A. Jennings, Chem. Phys. Lett. **78**, 589 (1981).

[11] U. Meier, H. H. Grotheer, and T. Just, Chem. Phys. Lett. **106**, 97 (1984).

[12] S. Dóbé, T. Berces, F. Temps, H. Gg. Wagner, and H. Ziemer, *25th International Symposium on Combustion* (The Combustion Institute, Pittsburgh, PA, 1994), pp. 775–781.

Cl + C_2H_5OH → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(8.75\pm0.95)\times10^{-11}$	295±2	Wallington *et al.*, 1988[1]	RR (a)
$(1.01\pm0.06)\times10^{-10}$	298±2	Nelson *et al.*, 1990[2]	RR (b)
$(8.3\pm1.8)\times10^{-11}$	295	Edelbuttel-Einhaus *et al.*, 1992[3]	RR (c)
Reviews and Evaluations			
9.4×10^{-11}	298	IUPAC, 1997[4]	(d)

Comments

(a) Cl atoms were generated by photolysis of Cl_2 in Cl_2–C_2H_5OH–C_2H_6–air (or N_2) mixtures at 1 bar total pressure. C_2H_5OH and C_2H_6 were monitored by GC and a rate coefficient ratio $k(Cl+C_2H_5OH)/k(Cl+C_2H_6)=1.483\pm0.160$ determined. Placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Cl atoms were generated by photolysis of Cl_2 or $COCl_2$ in Cl_2 (or $COCl_2$)–N_2 (or O_2)–ethanol–cyclohexane mixtures at 1 bar pressure. Concentrations of ethanol and cyclohexane were measured by GC, and the rate coefficient ratio is placed on an absolute basis by use of $k(Cl+\text{cyclohexane})=3.11\times10^{-10}$ cm^3 molecule^{-1} s^{-1}.[5]

(c) Isothermal discharge flow reactor at 1 mbar pressure, with molecular beam sampling and analysis by mass spectrometry. $k/k(Cl+C_2H_6)$ measured to be 1.4±0.3. Placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation). Supersedes earlier value reported from same laboratory.[6]

(d) Based on the results of Wallington *et al.*[1] and Nelson *et al.*[2]

Preferred Values

$k=9.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of those of Wallington *et al.*,[1] Nelson *et al.*,[2] and Edelbuttel-Einhaus *et al.*,[3] which are in good agreement.

References

[1] T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).
[2] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).
[3] J. Edelbuttel-Einhaus, K. Hoyermann, G. Rohde, and J. Seeba, *24th International Symposium on Combustion* (The Combustion Institute, Pittsburgh, PA, 1992), pp. 661–668.
[4] IUPAC, Supplement V, 1997 (see references in Introduction).
[5] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).
[6] T. Khatoon, J. Edelbuttel-Einhaus, K. Hoyermann, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **93**, 626 (1989).

Cl + n-C_3H_7OH → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.49\pm0.12)\times10^{-10}$	295±2	Wallington *et al.*, 1988[1]	RR (a)
$(1.49\pm0.07)\times10^{-10}$	298±2	Nelson *et al.*, 1990[2]	RR (b)
Reviews and Evaluations			
1.5×10^{-10}	298	IUPAC, 1997[3]	(c)

Comments

(a) Cl atoms were generated by photolysis of Cl_2 in Cl_2-n-C_3H_7OH–C_2H_6–air (or N_2) mixtures at 990 mbar (740 Torr) total pressure. n-C_3H_7OH and C_2H_6 were monitored by GC and a rate coefficient ratio $k(Cl+n\text{-}C_3H_7OH)/k(Cl+C_2H_6)=2.518\pm0.202$ determined. Placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Cl atoms were generated by the photolysis of Cl_2 or $COCl_2$ in Cl_2 (or $COCl_2$)–N_2 (or O_2)-*n*-propanol–cyclohexane mixtures at 1 bar pressure. Decay rates of *n*-propanol and cyclohexane were measured by GC, and the rate coefficient ratio placed on an absolute basis by use of k(Cl+cyclohexane)$=3.11\times10^{-10}$ cm^3 molecule^{-1} s^{-1}.[4]

(c) See Comments on Preferred Values.

Preferred Values

$k=1.5\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the data of Wallington *et al.*[1] and Nelson *et al.*,[2] which are in excellent agreement, and is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).
[2] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).
[4] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

$Cl + i\text{-}C_3H_7OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(8.40\pm0.35)\times10^{-11}$	298±2	Nelson *et al.*, 1990[1]	RR (a)
Reviews and Evaluations			
8.4×10^{-11}	298	IUPAC, 1997[2]	(b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 or $COCl_2$ in Cl_2 (or $COCl_2$)–isopropyl alcohol–cyclohexane–O_2 (or N_2) mixtures at 1 bar pressure. The decay rates of isopropyl alcohol and cyclohexane were measured, and rate coefficient ratio placed on an absolute basis by use of k(Cl+cyclohexane)$=3.11\times10^{-10}$ cm^3 molecule^{-1} s^{-1}.[3]

(c) See Comments on Preferred Values.

Preferred Values

$k=8.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

Based on the sole study of Nelson *et al.*,[1] and is identical to that in our previous evaluation, IUPAC, 1997.[2]

References

[1] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).
[2] IUPAC, Supplement V, 1997 (see references in Introduction).
[3] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

$$\mathrm{Cl + CH_3OOH \rightarrow HCl + CH_3O_2} \quad (1)$$

$$\mathrm{\rightarrow HCl + CH_2OOH} \quad (2)$$

$\Delta H°(1) = -72\ \mathrm{kJ{\cdot}mol^{-1}}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comment
Relative Rate Coefficients			
$(5.9 \pm 0.3) \times 10^{-11}$	295±2	Wallington *et al.*, 1990[1]	RR (a)
Reviews and Evaluations			
5.9×10^{-11}	298	IUPAC, 1997[2]	(b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2–N_2–CH_3OOH–C_2H_6 mixtures at 930 mbar (700 Torr) total pressure, and the CH_3OOH and C_2H_6 concentrations monitored by FTIR absorption spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of $k(\mathrm{Cl + C_2H_6}) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) See Comments on Preferred Values.

Preferred Values

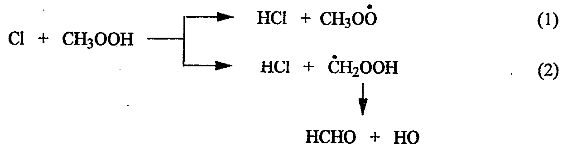
$k = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The sole study carried out to date is that of Wallington *et al.*[1] The reaction may occur by the two pathways:



and the formation of HO radicals may have led to secondar reactions involving HO radicals. Since the room temperatur rate coefficient for the Cl atom reaction with H_2O_2 is tw orders of magnitude lower than that for Cl+CH_3OOH,[2] it i expected that channel (2) will dominate. Wallington *et al.* concluded that secondary reactions involving HO radical did not contribute ⩾15% to the observed CH_3OOH con sumption. The cited uncertainty limits on the preferred val ues reflect this possibility of HO radical involvement in th Wallington *et al.*[1] study. The preferred value is identical t that in our previous evaluation, IUPAC, 1997.[2]

References

[1] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos Chem. **10**, 301 (1990).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$$\mathrm{Cl + HCOOH \rightarrow HCl + HCO_2} \quad (1)$$

$$\mathrm{\rightarrow HCl + COOH} \quad (2)$$

$\Delta H°(2) = -58\ \mathrm{kJ{\cdot}mol^{-1}}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comment
Relative Rate Coefficients			
$(2.15 \pm 0.12) \times 10^{-13}$	295±2	Wallington *et al.*, 1990[1]	RR (a,b)
$(1.83 \pm 0.10) \times 10^{-13}$	295±2	Wallington *et al.*, 1990[1]	RR (a,c)
Reviews and Evaluations			
2.0×10^{-13}	298	IUPAC, 1997[2]	(d)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2–air–HCOOH–CH_3Cl (or CH_4) mixtures at 930 mbar (700 Torr) total pressure. HCOOH and CH_3Cl (or CH_4) were monitored by FTIR absorption spectroscopy during the experiments.

(b) Relative to $k(Cl+CH_3Cl)$. Placed on an absolute basis by use of $k(Cl+CH_3Cl)=4.9\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.[2]

(c) Relative to $k(Cl+CH_4)$. Placed on an absolute basis by use of $k(Cl+CH_4)=9.9\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} (this evaluation).

(d) See Comments on Preferred Values.

Preferred Values

$k=2.0\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the rate coefficients obtained by Wallington *et al.*[1] relative to $k(Cl+CH_3Cl)$ and $k(Cl+CH_4)$, which are in good agreement, and is identical to that in our previous evaluation, IUPAC, 1997.[2]

Tyndall *et al.*[3] have observed that CO_2 is the sole carbon-containing product formed from this reaction in air or N_2 diluent, and conclude from comparison of the rate coefficients for the reactions of the Cl atom with HCOOH, CH_3COOH,[4] and CD_3COOH (Ref. 4) that reaction channel (2) dominates.

References

[1] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).
[2] IUPAC, Supplement V, 1997 (see references in Introduction).
[3] G. S. Tyndall, T. J. Wallington, and A. R. Potts, Chem. Phys. Lett. **186**, 149 (1991).
[4] S. Koch and G. K. Moortgat, Chem. Phys. Lett. **173**, 531 (1990).

$Cl + CH_3COOH \rightarrow HCl + CH_2COOH$ (1)

$\rightarrow HCl + CH_3COO$ (2)

$\Delta H°(2)=10.9$ $kJ\cdot mol^{-1}$

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

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.8\pm0.4)\times10^{-14}$	298±1	Koch and Moortgat, 1990[1]	RR (a)
Reviews and Evaluations			
2.8×10^{-14}	298	IUPAC, 1997[2]	(b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2–CH_3COOH–CH_4–N_2 mixtures at 1 bar total pressure. The concentrations of CH_3COOH and CH_4 were measured by IR absorption spectroscopy. The rate coefficient ratio of $k(Cl+CH_3COOH)/k(Cl+CH_4)=0.28\pm0.04$ is placed on an absolute basis by use of $k(Cl+CH_4)=1.0\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} (this evaluation). An analogous experiment using CD_3COOH yielded a rate coefficient of $k(Cl+CD_3COOH)=(7.5\pm0.2)\times10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}, indicating that the majority of the reaction proceeds by reaction channel (1).

(c) See Comments on Preferred Values.

Preferred Values

$k=2.8\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole study of Koch and Moortgat[1] and is identical to that in our previous evaluation, IUPAC, 1997.[2] The measured rate coefficient ratio of $k(Cl+CH_3COOH)/k(Cl+CD_3COOH)=3.7$ at (298±1) K[1] indicates that channel (1) dominates at 298 K.

References

[1] S. Koch and G. K. Moortgat, Chem. Phys. Lett. **173**, 531 (1990).
[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$Cl + CH_3ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comment
Relative Rate Coefficients			
$(2.42\pm0.02)\times10^{-13}$	298 ± 2	Nielsen *et al.*, 1991[1]	RR (a)
Reviews and Evaluations			
2.4×10^{-13}	298	IUPAC, 1997[2]	(b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2–CH_3ONO_2–C_2H_6–N_2 mixtures at 1 bar pressure. Concentrations of methyl nitrate and ethane were measured by GC and the rate coefficient ratio is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) See Comments on Preferred Values.

Preferred Values

$k=2.4\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

Based on the sole study of Nielsen *et al.*[1] and is identica to that in our previous evaluation, IUPAC, 1997.[2] The reaction probably occurs via H-atom abstraction from the –CH group.[1]

References

[1] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys Lett. **178**, 163 (1991).
[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$Cl + C_2H_5ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(5.5\pm0.8)\times10^{-12}$	295 ± 2	Wallington *et al.*, 1990[1]	RR (a)
$(3.95\pm0.15)\times10^{-12}$	298 ± 2	Nielsen *et al.*, 1991[2]	RR (b)
Reviews and Evaluations			
4.7×10^{-12}	298	IUPAC, 1997[3]	(c)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2–ethyl nitrate–C_2H_5Cl–air mixtures at 1 bar pressure. Ethyl nitrate and C_2H_5Cl were measured by GC, and a rate coefficient ratio of k(Cl+ethyl nitrate)/$k(Cl+C_2H_5Cl)=0.46\pm0.03$ determined. Combined with $k(Cl+C_2H_5Cl)/k(Cl+C_2H_6)=0.201\pm0.027$[4] and $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation), the rate coefficient cited in the table is obtained.

(b) Cl atoms were generated by the photolysis of Cl_2–ethyl nitrate–C_2H_6–N_2 mixtures at atmospheric pressure. Concentrations of ethyl nitrate and ethane were measured by GC, and the rate coefficient ratio placed on a absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) See Comments on Preferred Values.

Preferred Values

$k=4.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the data of Wallington *et al.*[1] and Nielsen *et al.*,[2] and is identical to that in our previous evaluation, IUPAC, 1997.[3] The reaction probably proceeds by H atom abstraction from the C–H bonds.[2]

References

[1] T. J. Wallington, M. M. Hinman, J. M. Andino, W. O. Siegl, and S. M. Japar, Int. J. Chem. Kinet. **22**, 665 (1990).
[2] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).
[4] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

Cl + n-$C_3H_7ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(3.17\pm0.47)\times10^{-11}$	295±2	Wallington *et al.*, 1990[1]	RR (a)
$(2.28\pm0.14)\times10^{-11}$	298±2	Nielsen *et al.*, 1991[2]	RR (b)
Reviews and Evaluations			
2.7×10^{-11}	298	IUPAC, 1997[3]	(c)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2–n-propyl nitrate–C_2H_5Cl–air mixtures at 1 bar pressure. n-Propyl nitrate and C_2H_5Cl concentrations were measured by GC and a rate coefficient ratio of $k(Cl+n\text{-propyl nitrate})/k(Cl+C_2H_5Cl)=2.67\pm0.16$ determined. Combined with $k(Cl+C_2H_5Cl)/k(Cl+C_2H_6)=0.201\pm0.027$[4] and $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation), the rate coefficient cited in the table is obtained.

(b) Cl atoms were generated by the photolysis of Cl_2 in Cl_2–n-propyl nitrate–C_2H_6–N_2 mixtures at 1 bar pressure. Concentrations of n-propyl nitrate and C_2H_6 were measured by GC, and the rate coefficient ratio is placed on an absolute basis by use of $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) See Comments on Preferred Values.

Preferred Values

$k=2.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the data of Wallington *et al.*[1] and Nielsen *et al.*[2] and is identical to that in our previous evaluation, IUPAC, 1997.[3] The reaction probably proceeds by H-atom abstraction from the C–H bonds.[2]

References

[1] T. J. Wallington, M. M. Hinman, J. M. Andino, W. O. Siegl, and S. M. Japar, Int. J. Chem. Kinet. **22**, 665 (1990).
[2] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).
[4] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

$Cl + i\text{-}C_3H_7ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(5.8\pm1.1)\times10^{-12}$	295 ± 2	Wallington *et al.*, 1990[1]	RR (a)
Reviews and Evaluations			
5.8×10^{-12}	298	IUPAC, 1997[2]	(b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2–isopropyl nitrate–C_2H_5Cl–air mixtures at 1 bar pressure. Concentrations of isopropyl nitrate and C_2H_5Cl were measured by GC, and a rate coefficient ratio of $k(Cl+\text{isopropyl nitrate})/k(Cl+C_2H_5Cl)=0.49\pm0.06$ determined. Combined with $k(Cl+C_2H_5Cl)/k(Cl+C_2H_6)=0.201\pm0.027$[3] and $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation), the rate coefficient cited in the table is obtained.

(b) See Comments on Preferred Values.

Preferred Values

$k=5.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole study of Wallington *et al.*,[1] and is identical to that in our previous evaluation, IUPAC, 1997.[2]

References

[1] T. J. Wallington, M. M. Hinman, J. M. Andino, W. O. Siegl, and S. M. Japar, Int. J. Chem. Kinet. **22**, 665 (1990).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

[3] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

$Cl + 1\text{-}C_4H_9ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(8.54\pm0.20)\times10^{-11}$	298	Nielsen *et al.*, 1991[1]	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2–n-butyl nitrate–C_2H_6–N_2 mixtures at 1 bar pressure. Concentrations of n-butyl nitrate and C_2H_6 were measured by GC, and the rate coefficient ratio placed on an absolute basis by use $k(Cl+C_2H_6)=5.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k=8.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

Based on the sole study of Nielsen *et al.*,[1] with expanded uncertainty limits.

References

[1] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).

$Cl + CH_3C(O)OONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.7 \pm 1.7) \times 10^{-13}$	298	Tsalkani *et al.*, 1988[1]	DF-EPR
Relative Rate Coefficients			
$<7 \times 10^{-15}$	295 ± 2	Wallington *et al.*, 1990[2]	RR (a)
Reviews and Evaluations			
$<1 \times 10^{-14}$	298	NASA, 1997[3]	(b)
$<2 \times 10^{-14}$	298	IUPAC, 1997[4]	(c)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2–air–$CH_3C(O)OONO_2$–CH_4 mixtures at 930 mbar (700 Torr) total pressure, with the $CH_3C(O)OONO_2$ and CH_4 concentrations being monitored by FTIR absorption spectroscopy. Upper limit to relative rate coefficient ratio placed on an absolute basis by use of $k(Cl+CH_4) = 9.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Based on results of Wallington *et al.*[2]

(c) See Comments on Preferred Values.

Preferred Values

$k < 2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the relative rate coefficient measurement of Wallington *et al.*,[2] in which no reaction of $CH_3C(O)OONO_2$ was observed in the presence of Cl atoms. In both the relative rate study of Wallington *et al.*[2] and the absolute rate study of Tsalkani *et al.*,[1] the major impurity in the $CH_3C(O)OONO_2$ samples would be the C_{12} or C_{13} alkane solvent, respectively. While this was of no consequence in the relative rate study of Wallington *et al.*,[2] the presence of ~0.1% tridecane in the $CH_3C(O)OONO_2$ sample used by Tsalkani *et al.*[1] could account for the Cl reaction rate observed; their $CH_3C(O)OONO_2$ sample was >99% pure from IR measurements. The upper limit cited here is a factor of ~3 higher than measured by Wallington *et al.*[2] to allow for higher uncertainties, and is identical to that in our previous evaluation, IUPAC, 1997.[4]

References

[1] N. Tsalkani, A. Mellouki, G. Poulet, G. Toupance, and G. Le Bras, J. Atmos. Chem. **7**, 409 (1988).

[2] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

[3] NASA Evaluation No. 12, 1997 (see references in Introduction).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$Cl + CH_3CN \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 2.0 \times 10^{-15}$	298	Kurylo and Knable, 1984[1]	FP-RF
$3.46 \times 10^{-11} \exp[-(2785 \pm 115)/T]$	478–723	Poulet *et al.*, 1984[2]	DF-MS (a)
$(8.89 \pm 1.24) \times 10^{-15}$	295		
$(1.24 \pm 0.20) \times 10^{-14}$	296	Tyndall *et al.*, 1996[3]	PLP-RF
Relative Rate Coefficients			
$8 \times 10^{-11} \exp(-3000/T)$	370–413	Olbregts, Brasseur, and Arijs, 1984[4]	RR (b)
$1.7 \times 10^{-11} \exp[-(2140 \pm 200)/T]$	274–345	Tyndall *et al.*, 1996[3]	RR (c)
$(1.22 \pm 0.15) \times 10^{-14}$	296		
Reviews and Evaluations			
$1.6 \times 10^{-11} \exp(-2140/T)$	270–350	NASA, 1997[5]	(d)
$\leq 2.0 \times 10^{-15}$	298	IUPAC, 1997[6]	(e)

Comments

(a) Data were obtained over the range 295–723 K, and a curved Arrhenius plot was observed.

(b) Relative formation rates of products were monitored in a competitive chlorination system between CH_3CN and $CHCl_3$. Placed on an absolute basis by use of $k(Cl+CHCl_3)=1.15\times10^{-11}\exp(-1686/T)$ cm^3 $molecule^{-1}$ s^{-1}.

(c) Relative decay rates of CH_3CN and the reference gas were monitored by FTIR. For the temperature dependent study the reference compound was CH_4. In a completely independent system, relative values at 296 K were also derived using as the reference compound CD_4, CF_3CCl_2H, or CH_4. Based on three independent determinations by both absolute and relative rate methods the authors derived the value $k=(1.15\pm0.20)\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 296 K and the Arrhenius expression $k=1.6\times10^{-11}\exp[-(2140\pm200)/T]$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 274–345 K. Product studies showed that at room temperature reaction proceeds predominantly, if not exclusively, by H-atom abstraction.

(d) Based on the results of Tyndall *et al.*[3]

(e) Based on the upper limit determined by Kurylo and Knable.[1]

Preferred Values

$k=1.2\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$k=1.6\times10^{-11}\exp(-2140/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 270–350 K.

Reliability

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

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The preferred values are based on the results reported by Tyndall *et al.*[3] The results of this study over a wide range of experimental conditions, using both relative and absolute rate methods, are preferred over results of earlier studies by Kurylo and Knable,[1] Poulet *et al.*,[2] and Olbregts *et al.*[4] In the study of Tyndall *et al.*,[3] the room-temperature rate coefficient was found to be independent of pressure over the range 7–930 mbar (5–700 Torr). Also in this study it was shown that at room temperature the reaction proceeds predominantly by H-atom abstraction.[3]

References

[1] M. J. Kurylo and G. L. Knable, J. Phys. Chem. **88**, 3305 (1984).

[2] G. Poulet, G. Laverdet, J. L. Jourdain, and G. Le Bras, J. Phys. Chem. **88**, 6259 (1984).

[3] G. S. Tyndall, J. J. Orlando, T. J. Wallington, J. Sehested, and O. J. Nielsen, J. Phys. Chem. **100**, 660 (1996).

[4] J. Olbregts, G. Brasseur, and E. Arijs, J. Photochem. **24**, 315 (1984).

[5] NASA Evaluation No. 12, 1997 (see references in Introduction).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

$Br + HCHO \rightarrow HBr + HCO$

$\Delta H^\circ=3.5$ $kJ\cdot mol^{-1}$

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.44\times10^{-11}\exp[-(750\pm112)/T]$	223–480	Nava, Michael, and Stief, 1981[1]	FP-RF
$(1.08\pm0.10)\times10^{-12}$	298		
$2.97\times10^{-11}\exp[-(1015\pm70)/T]$	295–480	Poulet, Laverdet, and Le Bras, 1981[2]	DF-MS
$(9.4\pm0.8)\times10^{-13}$	295		
Reviews and Evaluations			
$1.7\times10^{-11}\exp(-800/T)$	223–480	NASA, 1997[3]	(a)
$1.7\times10^{-11}\exp(-800/T)$	220–480	IUPAC, 1997[4]	(b)

Comments

(a) Based on a least-squares analysis of the absolute rate coefficient data of Nava *et al.*[1] and Poulet *et al.*[2]

(b) See Comments on Preferred Values.

Preferred Values

$k=1.1\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$k=1.7\times10^{-11}\exp(-800/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 220–480 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.

$\Delta(E/R)=\pm250$ K.

Comments on Preferred Values

The preferred rate expression is obtained from a least-squares analysis of the absolute rate coefficient data of Nava *et al.*[1] and Poulet *et al.*,[2] which are in reasonably good agreement. The preferred Arrhenius expression is identical to that in our previous evaluation, IUPAC, 1997.[4]

References

[1] D. F. Nava, J. V. Michael, and L. J. Stief, J. Phys. Chem. **85**, 1896 (1981).
[2] G. Poulet, G. Laverdet, and G. Le Bras, J. Phys. Chem. **85**, 1892 (1981).
[3] NASA Evaluation No. 12, 1997 (see references in Introduction).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$Br + CH_3CHO \rightarrow HBr + CH_3CO$

$\Delta H° = 7.6\ kJ\cdot mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.5) \times 10^{-12}$	300	Islam, Marshall, and Benson, 1984[1]	(a)
$1.51 \times 10^{-11} \exp[-(364 \pm 41)/T]$	255–400	Nicovich, Shackelford, and Wine, 1990[2]	LP-RF
4.45×10^{-12}	298		
Relative Rate Coefficients			
$(3.7 \pm 0.1) \times 10^{-12}$	298	Niki *et al.*, 1985[3]	RR (b)
Reviews and Evaluations			
$1.3 \times 10^{-11} \exp(-360/T)$	250–400	IUPAC, 1997[4]	(c)

Comments

(a) Very low pressure reactor study. Br atoms were generated by microwave discharge of Br_2 in helium, with mass spectrometric detection of reactants and products.

(b) Br atoms were generated by photolysis of Br_2 at 350–600 nm in 930 mbar (700 Torr) total pressure of N_2. The rate coefficient was determined relative to that for the reaction of Br atoms with HCHO, with $k(Br+CH_3CHO)/k(Br+HCHO) = 3.39 \pm 0.10$. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Br+HCHO) = 1.1 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$ (this evaluation).

(c) See Comments on Preferred Values.

Preferred Values

$k = 3.9 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k = 1.3 \times 10^{-11} \exp(-360/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 250–400 K.

Reliability

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

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

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute rate coefficients of Islam *et al.*[1] and Nicovich *et al.*[2] and the relative rate coefficient of Niki *et al.*[3] The temperature dependence is that measured by Nicovich *et al.*,[2] with the *A* factor being adjusted to yield the 298 K preferred value. The preferred room temperature rate coefficient is consistent with the relative rate studies of Barnes *et al.*[5] and Wallington *et al.*[6] (which do not provide definitive data concerning the rate constant for the reaction of Br atoms with CH_3CHO). The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

References

[1] T. S. A. Islam, R. M. Marshall, and S. W. Benson, Int. J. Chem. Kinet. **16**, 1161 (1984).
[2] J. M. Nicovich, C. J. Shackelford, and P. H. Wine, J. Photochem. Photobiol. A: Chem. **51**, 141 (1990).
[3] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **17**, 525 (1985).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).
[5] I. Barnes, V. Bastian, K. H. Becker, R. Overath, and Z. Tong, Int. J. Chem. Kinet. **21**, 499 (1989).
[6] T. J. Wallington, L. M. Skewes, W. O. Siegl, and S. M. Japar, Int. J. Chem. Kinet. **21**, 1069 (1989).

HCHO + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
HCHO+$h\nu \rightarrow$H+HCO (1)	369.7	324
$\rightarrow H_2$+CO (2)	−1.9	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
240–360	Moortgat and Schneider[1]	(a)
300–360	Cantrell *et al.*, 1990[2]	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi, \phi_2/\phi$	253–353	Moortgat, Seiler, and Warneck, 1983[3]	(c)

Comments

(a) Cross-sections measured at 220 and 298 K at different concentrations of HCHO and extrapolated to zero concentration. This extrapolation procedure yielded virtually identical cross-sections with and without added N_2.

(b) High-resolution FT spectroscopy used to measure cross-sections as a function of temperature (223–293 K). Values at different concentrations of HCHO were extrapolated to zero concentration.

(c) Quantum yields of CO and H_2 were measured as a function of wavelength for HCHO in low concentration in air. Previous results on the pressure and temperature dependences of ϕ_1 and ϕ_2 were confirmed.[4]

Absorption cross-sections at 285 K[a]

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
240	0.064	271	1.789	302	1.064	333	0.215
241	0.056	272	1.227	303	3.201	334	0.171
242	0.105	273	0.645	304	6.902	335	0.143
243	0.115	274	0.656	305	4.914	336	0.194
244	0.082	275	2.232	306	4.632	337	0.417
245	0.103	276	2.416	307	2.100	338	2.360
246	0.098	277	1.402	308	1.494	339	4.712
247	0.135	278	1.050	309	3.407	340	2.481
248	0.191	279	2.548	310	1.950	341	0.759
249	0.282	280	2.083	311	0.521	342	0.681
250	0.205	281	1.475	312	1.120	343	1.953
251	0.170	282	0.881	313	1.116	344	1.137
252	0.288	283	1.066	314	4.747	345	0.323
253	0.255	284	4.492	315	5.247	346	0.113
254	0.255	285	3.592	316	2.899	347	0.066
255	0.360	286	1.962	317	5.373	348	0.122
256	0.509	287	1.295	318	2.975	349	0.032
257	0.339	288	3.356	319	0.918	350	0.038
258	0.226	289	2.838	320	1.262	351	0.104
259	0.504	290	1.304	321	1.529	352	0.713
260	0.505	291	1.746	322	0.669	353	2.212
261	0.549	292	0.832	323	0.345	354	1.536
262	0.520	293	3.727	324	0.816	355	0.676
263	0.933	294	6.535	325	1.850	356	0.135
264	0.823	295	3.950	326	5.950	357	0.036
265	0.430	296	2.333	327	3.485	358	0.0057
266	0.495	297	1.513	328	1.087	359	0.058
267	1.239	298	4.037	329	3.353	360	0.082
268	1.110	299	2.871	330	3.321		
269	0.878	300	0.871	331	1.073		
270	0.936	301	1.715	332	0.289		

[a] Average over 0.5 nm wavelength intervals centered at the cited wavelength [G. K. Moortgat and W. Schneider (unpublished data)].

Absorption cross-sections[a] as a function of temperature (223–293 K)[b]

	σ/cm^2			
λ/nm	223 K	293 K	Intercept (273 K)	Temp. gradient
301.25	1.38E−20	1.36E−20	1.37E−20	−2.10E−24
303.75	4.67E−20	4.33E−20	4.43E−20	−4.73E−23
306.25	3.32E−20	3.25E−20	3.27E−20	−1.06E−23
308.75	2.27E−20	2.22E−20	2.24E−20	−7.24E−24
311.25	7.58E−21	9.31E−21	8.82E−21	2.48E−23
313.75	3.65E−20	3.40E−20	3.47E−20	−3.64E−23
316.25	4.05E−20	3.89E−20	3.94E−20	−2.30E−23
318.75	1.66E−20	1.70E−20	1.69E−20	6.59E−24
321.25	1.24E−20	1.13E−20	1.16E−20	−1.52E−23
323.75	4.65E−21	4.73E−21	4.71E−21	1.18E−24
326.25	5.06E−20	4.44E−20	4.61E−20	−8.86E−23
328.75	2.44E−20	2.29E−20	2.43E−20	−2.15E−23
331.25	1.39E−20	1.28E−20	1.31E−20	−1.53E−23
333.75	9.26E−22	1.23E−21	1.14E−21	4.32E−24
336.25	1.27E−21	1.31E−21	1.30E−21	5.03E−25
338.75	3.98E−20	3.36E−20	3.45E−20	−8.96E−23
341.25	8.05E−21	9.36E−21	8.98E−21	1.86E−23
343.75	1.44E−20	1.26E−20	1.31E−20	−2.64E−23
346.25	3.39E−23	7.10E−22	5.18E−22	9.57E−24
348.75	9.05E−23	3.97E−22	3.10E−22	4.38E−24
351.25	1.69E−21	2.35E−21	2.16E−21	9.48E−24
353.75	1.83E−20	1.55E−20	1.63E−20	−4.05E−23
356.25	3.54E−22	1.25E−21	9.19E−22	1.27E−23

[a] 2.5 nm interval centered at given λ.

[b] At any temperature within the range 223–293 K, σ can be calculated from the listed gradient (slope) and intercept fit parameters, with $\sigma = (\text{slope} \times T(^\circ\text{C}) + \text{intercept})$ [C. A. Cantrell, J. A. Davidson, A. H. McDaniel, R. E. Shetter, and J. G. Calvert, J. Phys. Chem. **94**, 3902 (1990)].

Quantum yields in air at 1 bar and 298 K

λ/nm	ϕ_1	ϕ_2
240	0.27	0.49
250	0.29	0.49
260	0.30	0.49
270	0.38	0.43
280	0.57	0.32
290	0.73	0.24
300	0.78	0.21
310	0.78	0.22
320	0.62	0.38
330	0.27	0.66
340	0.00	0.56
350	0.00	0.21
360	0.00	0.03

Comments on Preferred Values

The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5] The recommended absorption cross-sections are those of Moortgat and Schneider[1] for $\lambda \leq 300$ nm and of Cantrell *et al.*[2] for $\lambda = 301-356$ nm, the latter providing a temperature dependence over the range 223–293 K.

Measurements of the quantum yields by Horowitz and Calvert,[6] Clark *et al.*,[7] Tang *et al.*,[8] Moortgat and Warneck,[4] and Moortgat *et al.*[3] are in good agreement. The preferred values are those determined by Moortgat *et al.*[3] and apply to atmospheric pressure and 298 K. For wavelengths longer than about 330 nm the quantum yields of CO and H_2 production have been shown to be pressure and temperature dependent.[3]

The problem of understanding the measured quantum yields and branching ratios, $Y_2 = \phi_2/(\phi_1 + \phi_2)$, remains unresolved. If the photochemistry were governed by a sequence of light absorption into the first excited electronic state, internal conversion to the electronic ground state, and subsequent competition of the reactions $HCHO^* \rightarrow H + HCO$ and $HCHO^* \rightarrow H_2 + CO$, then the measured values of Y_2 for $\lambda \leq 300$ nm would be difficult to interpret. Simulations[9] of the rates of the competing processes of HCHO* and measurements of the product yields in molecular beams[10] indicates that the radical channel (1), $HCHO^* \rightarrow H + HCO$ dominates for $\lambda \leq 300$ nm, with $Y_2 < 0.1$ at 284 nm.[10] An analysis of the details of the photophysical processes[11] has failed to resolve this discrepancy with the macroscopic photochemical observations. The branching ratios for ≤ 300 nm should therefore be treated with caution.

References

[1] G. K. Moortgat and W. Schneider (unpublished data).

[2] C. A. Cantrell, J. A. Davidson, A. H. McDaniel, R. E. Shetter, and J. G. Calvert, J. Phys. Chem. **94**, 3902 (1990).

[3] G. K. Moortgat, W. Seiler, and P. Warneck, J. Chem. Phys. **78**, 1185 (1983).

[4] G. K. Moortgat and P. Warneck, J. Chem. Phys. **70**, 3639 (1979).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

[6] A. Horowitz and J. G. Calvert, Int. J. Chem. Kinet. **10**, 805 (1978).

[7] J. H. Clark, C. B. Moore, and N. S. Nogar, J. Chem. Phys. **68**, 1264 (1978).

[8] K. Y. Tang, P. W. Fairchild, and E. K. C. Lee, J. Phys. Chem. **83**, 569 (1979).

[9] J. Troe, J. Phys. Chem. **88**, 4375 (1984).

[10] P. Ho, D. J. Bamford, R. J. Buss, Y. T. Lee, and C. B. Moore, J. Chem. Phys. **76**, 3630 (1982).

[11] C. B. Moore and J. C. Weisshaar, Ann. Rev. Phys. Chem. **34**, 325 (1983).

$CH_3CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CHO + h\nu \rightarrow CH_4 + CO$ (1)	−19.5	
$\rightarrow CH_3 + HCO$ (2)	355.3	337
$\rightarrow CH_3CO + H$ (3)	373.8	320

Absorption cross-sections

Wavelength range/nm	Reference	Comments
202–365	Martinez *et al.*, 1992[1]	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement		Wavelength range/nm	Reference	Comments
$\phi_1 = 0.46$	$\phi_2 = 0.31$	260	Meyrahn, Moortgat, and Warneck, 1982[2]	(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		
$\phi_1 = 0.0$	$\phi_2 = 0.37$	305		
$\phi_1 = 0.0$	$\phi_2 = 0.28$	310		
$\phi_1 = 0.0$	$\phi_2 = 0.10$	320		
$\phi_1 = 0.0$	$\phi_2 = 0.04$	325		
$\phi_1 = 0.0$	$\phi_2 = 0.00$	330		

Comments

(a) Double beam spectrophotometric measurements with 10 cm pathlength. Data obtained at 0.1 nm intervals with 0.5 nm resolution. Argon–acetaldehyde mixtures used at a total pressure of 133 mbar and several acetaldehyde pressures in the range 1.3–2.6 mbar. Cross-sections tabulated are averages over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region centered on the corresponding wavelength (see Preferred Values).

(b) Quantum yields of CH_4 and CO determined from the photolysis of 100 ppm of CH_3CHO in air or N_2 at a total pressure of 1 bar. H_2 was found only in trace quantities and hence it was concluded that the photolytic channel giving $CH_3CO + H$ ($\lambda_{threshold} = 320$ nm) is negligible. Quantum yield data based on the assumption that $\phi_1 + \phi_2 + \phi_a = 1$, where ϕ_a refers to the quenching process $CH_3CHO^* + M \rightarrow CH_3 + CHO + M$. Quantum yield data at 1 bar pressure were found to be independent of the diluent, N_2, or air. ϕ_{CO} both in N_2 and in air increased as the total pressure was lowered.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$
202	0.056	297	4.38	334	0.363
206	0.053	298	4.41	335	0.350
210	0.049	299	4.26	336	0.238
214	0.048	300	4.16	337	0.222
218	0.052	301	3.99	338	0.205
222	0.065	302	3.86	339	0.219
226	0.096	303	3.72	340	0.150
230	0.151	304	3.48	341	0.074
234	0.241	305	3.42	342	0.042
238	0.375	306	3.42	343	0.031
242	0.564	307	3.36	344	0.026
246	0.818	308	3.33	345	0.021
250	1.128	309	3.14	346	0.019
254	1.524	310	2.93	347	0.015
258	1.994	311	2.76	348	0.016
262	2.44	312	2.53	349	0.010
266	3.05	313	2.47	350	0.008
270	3.42	314	2.44	351	0.007
274	4.03	315	2.20	352	0.006
278	4.19	316	2.04	353	0.005
280	4.50	317	2.07	354	0.005
281	4.69	318	1.979	355	0.004
282	4.72	319	1.874	356	0.005
283	4.75	320	1.723	357	0.003
284	4.61	321	1.484	358	0.004
285	4.49	322	1.402	359	0.002
286	4.44	323	1.244	360	0.003
287	4.59	324	1.091	361	0.002
288	4.72	325	1.136	362	0.001
289	4.77	326	1.074	363	0.000
290	4.89	327	0.858	364	0.000
291	4.78	328	0.747	365	0.000
292	4.68	329	0.707		
293	4.53	330	0.688		
294	4.33	331	0.588		
295	4.27	332	0.530		
296	4.24	333	0.398		

Quantum yields in air at 1 bar and 298 K

λ/nm	ϕ_1	ϕ_2
260	0.46	0.31
270	0.31	0.39
280	0.05	0.58
290	0.01	0.53
295	0.00	0.48
300		0.43
305		0.37
310		0.29
315		0.17
320		0.10
325		0.04
330		0.00

Comments on Preferred Values

The preferred absorption cross-sections are from the extensive measurements of Martinez *et al.*[1] Over the wavelength region 260–320 nm these cross-sections are within 5% of the data of Calvert and Pitts[3] and Weaver *et al.*[4]

The preferred values for the quantum yields are those obtained by Meyrahn *et al.*[2] Atkinson and Lloyd[5] have evaluated the quantum yield data of Meyrahn *et al.*[2] and of Horowitz and Calvert[6] and derive values in very close agreement with those recommended here.

The preferred values for both the absorption cross sections and quantum yields are identical to those given in our previous evaluation, IUPAC, 1997.[7]

References

[1] R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn, and J. A. Joens, Atmos. Environ. **26A**, 785 (1992).

[2] H. Meyrahn, G. K. Moortgat, and P. Warneck, presented at the XVth Informal Conference on Photochemistry, Stanford Research Institute, Stanford, California, July 1982.

[3] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).

[4] J. Weaver, J. Meagher, and J. Heicklen, J. Photochem. **6**, 111 (1976).

[5] R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).

[6] A. Horowitz and J. G. Calvert, J. Phys. Chem. **86**, 3105 (1982).

[7] IUPAC, Supplement V, 1997 (see references in Introduction).

$C_2H_5CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$C_2H_5CHO \rightarrow C_2H_5+HCO$	(1)	351.4	340
$\rightarrow C_2H_6+CO$	(2)	−7.1	
$\rightarrow C_2H_4+HCHO$	(3)	131.0	913
$\rightarrow CH_3+CH_2CHO$	(4)	344.3	347

Absorption cross-section data

Wavelength range/nm	Reference	Comment
202–365	Martinez *et al.*, 1992[1]	(a)

Quantum yield data ($\phi=\phi_1+\phi_2+\phi_3+\phi_4$)

Measurement	Wavelength range/nm	Reference	Comment
$\phi_1=0.89$	294	Heicklen *et al.*, 1986[2]	(b)
$\phi_1=0.50$	302		
$\phi_1=0.26$	325		
$\phi_1=0.15$	334		

Comments

(a) Cross-sections are the average cross-section over a 1 nm ($\lambda>280$ nm) or 4 nm ($\lambda<280$ nm) region centered at the corresponding wavelength (see Preferred Values).

(b) Flash photolysis of C_2H_5CHO in the presence of air and steady-state photolysis of C_2H_5CHO in the presence of O_2 at 263 or 298 K. Quantum yields of CO and C_2H_6 were measured as a function of wavelength and of O_2 pressure. From the proposed mechanism it was deduced that $\phi_1=(\phi_\infty-\phi_{C_2H_6})$. The values of ϕ quoted are for 1 bar air.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$
202	0.049	295	5.57	330	0.575
206	0.049	296	5.37	331	0.494
210	0.057	297	5.16	332	0.466
214	0.069	298	5.02	333	0.430
218	0.080	299	5.02	334	0.373
222	0.091	300	5.04	335	0.325
226	0.115	301	5.09	336	0.280
230	0.163	302	5.07	337	0.230
234	0.257	303	4.94	338	0.185
238	0.407	304	4.69	339	0.166
242	0.622	305	4.32	340	0.155
246	0.909	306	4.04	341	0.119
250	1.287	307	3.81	342	0.076
254	1.745	308	3.65	343	0.045
258	2.25	309	3.62	344	0.031
262	2.88	310	3.60	345	0.025
266	3.43	311	3.53	346	0.019
270	4.12	312	3.50	347	0.016
274	4.59	313	3.32	348	0.014
278	5.17	314	3.06	349	0.013
280	5.16	315	2.77	350	0.010
281	5.21	316	2.43	351	0.008
282	5.35	317	2.18	352	0.007
283	5.57	318	2.00	353	0.005
284	5.78	319	1.864	354	0.004
285	5.86	320	1.831	355	0.002
286	5.82	321	1.777	356	0.001
287	5.72	322	1.662	357	0.001
288	5.59	323	1.577	358	0.000
289	5.52	324	1.488	359	0.000
290	5.56	325	1.300	360	0.000
291	5.68	326	1.129	361	0.000
292	5.81	327	0.996	362	0.000
293	5.88	328	0.828	363	0.000
294	5.80	329	0.685	364	0.000
				365	0.000

Quantum yields in air at 1 bar and 298 K

λ/nm	ϕ_1
294	0.89
302	0.85
313	0.50
325	0.26
334	0.15

Comments on Preferred Values

The preferred absorption cross-sections are from the measurements of Martinez *et al.*[1] Over the wavelength region 260–320 nm these cross-sections are within 5% of our earlier recommendations based on the data of Calvert and Pitts.[3]

The preferred values of the quantum yields for the photodissociation yielding C_2H_5 radicals are taken from the study of Heicklen *et al.*,[2] and refer to photolysis in air at a total pressure of 1 atm. No explanation has been put forward to account for the large differences in the reported values of ϕ_1 as a function of wavelength.[4,5]

The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[6]

References

[1] R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn, and J. A. Joens, Atmos. Environ. **26A**, 785 (1992).

[2] J. Heicklen, J. Desai, A. Bahta, C. Harper, and R. Simonaitis, J. Photochem. **34**, 117 (1986).

[3] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).

[4] P. B. Shepson and J. Heicklen, J. Photochem. **18**, 169 (1982).

[5] P. B. Shepson and J. Heicklen, J. Photochem. **19**, 215 (1982).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

$(CHO)_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$(CHO)_2 + h\nu \rightarrow H_2 + 2CO$	(1)	−9.1	
$\rightarrow 2HCO$	(2)	298.1	401
$\rightarrow HCHO + CO$	(3)	−7.2	
$\rightarrow H + CO + HCO$	(4)	362.5	330

Absorption cross-section data

Wavelength range/nm	Reference	Comments
230–462	Plum *et al.*, 1983[1]	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi = 0.029 \pm 0.018$	325–470	Plum *et al.*, 1983[1]	(b)
$\phi(HCO) = 0.8 \pm 0.4$	308	Langford and Moore, 1984[2]	(c)
$\phi(HCO) = 0.42 \pm 0.22$	193	Zhu, Kellis, and Ding, 1996[3]	(d)
$\phi(HCO) = 0.54 \pm 0.24$	248		
$\phi(HCO) = 0.70 \pm 0.30$	308		
$\phi(HCO) = 1.5 \pm 0.6$	351		

Comments

(a) Conventional spectrophotometric study (Cary 17-D) using glyoxal pressures of ~4–17 mbar.

(b) Rate of photolysis of glyoxal in air mixtures at atmospheric pressure measured in an environmental chamber. The quantum yield for the photodissociation of glyoxal was obtained by comparison of the measured rate of removal of glyoxal with the rate of photolysis of NO_2 under similar experimental conditions.

(c) Laser photolysis of 5.3 mbar glyoxal in 1.3 bar N_2 at 295 K. HCO product determined by time-resolved laser resonance absorption. Quantum yield determined by comparing the HCO radical absorption observed with the same signals following HCHO and $(CHO)_2$ photolyses.

(d) Excimer laser photolysis of flowing glyoxal–N_2 mixtures. [HCO] monitored by time-resolved cavity ring-down spectroscopy. Yields of HCO determined by comparison of absorption with signals from photolysis of formaldehyde–N_2 mixtures under similar conditions. Incident light intensities were measured by a Joulemeter calibrated by chemical actinometry. The HCO quantum yields were found to be independent of glyoxal pressure, total pressure (26–470 mbar), and light intensity.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$
230.5	0.30	390	3.14	427	10.76
235	0.30	391	3.45	428	16.65
240	0.42	392	3.25	429	4.06
245	0.57	393	2.23	430	5.07
250	0.84	394	2.64	431	4.87
255	1.15	395	3.04	432	4.06
260	1.45	396	2.64	433	3.65
265	1.88	397	2.44	434	4.06
270	2.30	398	3.25	435	5.07
275	2.60	399	3.04	436	8.12
280	2.87	400	2.84	437	5.28
285	3.33	401	3.25	438	10.15
290	3.18	402	4.46	439	7.71
295	3.33	403	5.28	440	24.76
300	3.60	404	4.26	441	8.12
305	2.76	405	3.05	442	6.09
310	2.76	406	3.05	443	7.51
312.5	2.88	407	2.84	444	9.34
315	2.30	408	2.44	445	11.37
320	1.46	409	2.84	446	5.28
325	1.15	410	6.09	447	2.44
327.5	1.46	411	5.27	448	2.84
330	1.15	412	4.87	449	3.86
335	0.30	413	8.32	450	6.09
340	0.00	414	7.51	451	10.96
345	0.00	415	8.12	452	12.18
350	0.00	416	4.26	453	23.95
355	0.00	417	4.87	454	17.05
360	0.23	418	5.89	455	40.60
365	0.30	419	6.70	456	10.14
370	0.80	420	3.86	457	1.63
375	1.03	421	5.68	458	1.22
380	1.72	422	5.28	459	0.41
382	1.57	423	10.55	460	0.41
384	1.49	424	6.09	461	0.20
386	1.49	425	7.31	462	0.00
388	2.87	426	11.77		

Comments on Preferred Values

The preferred values for the absorption cross-sections are those determined by Plum *et al.*,[1] and are unchanged from our previous evaluation, IUPAC, 1997.[4] Zhu *et al.*[3] have recently measured the cross-sections at 193, 248, 308, and 351 nm. Where comparison is possible with those of Plum *et al.*,[1] there is good agreement at 308 nm, but at 248 and 351 nm the values obtained by Zhu *et al.*[3] are substantially higher. Further measurements are desirable to resolve these differences.

There are insufficient data on quantum yields to recommend values as a function of wavelength under atmospheric conditions. The ''effective'' quantum yield of $\phi=0.029$ reported by Plum *et al.*[1] is valid only for the particular spectral distribution used in their study. They measured $(\phi\sigma)$ integrated over the range 325–470 nm and this may be used to calculate the rate of photolysis of glyoxal under tropospheric conditions within that spectral region. Both Zhu *et al.*[3] and Langford and Moore[2] obtain a value of $\phi_2\approx0.4$ at 308 nm. It is recommended that this value be used in calculations of photolysis rates at shorter wavelengths.

References

[1] C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., Environ. Sci. Technol. **17**, 479 (1983).

[2] A. O. Langford and C. B. Moore, J. Chem. Phys. **80**, 4211 (1984).

[3] L. Zhu, D. Kellis, and C.-F. Ding, Chem. Phys. Lett. **257**, 487 (1996).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3COCHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CH_3COCHO + h\nu \rightarrow CH_4 + 2CO$	(1)	−78.8	
$\rightarrow CH_3CO + HCO$	(2)	250.8	478
$\rightarrow CH_3CHO + CO$	(3)	−59.2	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–480	Meller *et al.*, 1991[1]	(a)
205–480	Staffelbach *et al.*, 1995[2]	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ=0.005	410–418	Staffelbach *et al.*, 1995[2]	(c)
ϕ=0.055	355–480		
ϕ=0.07	280–420		
ϕ=0.08	280–420		
ϕ=0.14	240–420		

Comments

(a) Measured over the range 220–480 nm by conventional UV spectroscopy in a cell of path length 63 cm. Light was detected by a diode array camera and the spectral resolution was 0.07 nm. As well as using methylglyoxal prepared external to the cell, methylglyoxal was generated *in situ* by the Cl atom-initiated modulated photooxidation of hydroxyacetone and the cross-sections were measured over the range 390–460 nm in these *in situ* studies.

(b) Cross-sections measured in a 90 cm cell using a diode array spectrometer. The spectral resolution was estimated to be 0.6 nm. Pressures in the range 0.13–8.0 mbar were used and measurements were made at 248, 273, and 298 K.

(c) Low concentrations of methylglyoxal in an $O_2(20\%)-N_2(80\%)$ mixture at 1 bar were photolyzed with an Xe arc equipped with filters to isolate wavelength regions. Products (HCHO, CH_3COOH, CH_3COO_2H, CH_3OH, HCOOH, CO, CO_2) were monitored by FTIR. Light intensity calibrated by photolysis of $Cl_2-CH_3OH-O_2-N_2$ mixture. Quantum yields were derived by modeling product yields taking into account a number of important secondary reactions.

Preferred Values

Absorption cross-sections at 298 K at 5 nm intervals between 225 and 410 nm

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2
225	1.268	320	1.511
230	1.477	325	0.938
235	1.803	330	0.652
240	2.071	335	0.482
245	2.304	340	0.323
250	2.612	345	0.300
255	2.859	350	0.394
260	3.280	355	0.560
265	3.618	360	0.695
270	4.159	365	1.077
275	4.413	370	1.475
280	4.877	375	1.911
285	4.719	380	2.429
290	4.838	385	3.221
295	4.362	390	4.029
300	3.754	395	4.732
305	3.361	400	5.664
310	2.365	405	6.923
315	1.891	410	8.459

Preferred Values

Absorption cross-sections at 298 K at 1 nm intervals between 401 and 475 nm

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²
401	5.90	439	11.01
402	6.07	440	9.94
403	6.35	441	10.39
404	6.54	442	10.20
405	6.91	443	10.17
406	7.20	444	11.17
407	7.58	445	9.61
408	7.94	446	8.90
409	8.12	447	9.84
410	8.52	448	9.18
411	8.63	449	10.13
412	9.07	450	8.67
413	9.37	451	6.34
414	9.62	452	6.33
415	9.68	453	6.08
416	9.71	454	4.46
417	10.04	455	3.69
418	10.07	456	3.08
419	10.12	457	2.46
420	10.21	458	1.81
421	10.34	459	1.28
422	10.51	460	0.914
423	10.45	461	0.795
424	10.15	462	0.642
425	10.34	463	0.479
426	10.24	464	0.332
427	9.84	465	0.268
428	10.01	466	0.227
429	9.94	467	0.187
430	10.41	468	0.160
431	10.53	469	0.133
432	9.79	470	0.108
433	10.64	471	0.099
434	10.54	472	0.089
435	10.81	473	0.077
436	11.13	474	0.067
437	9.99	475	0.062
438	10.59		

Quantum yields in air at 1 bar and 298 K

λ/nm	φ
410–418	0.005
355–480	0.055
280–420	0.08
240–420	0.14

Comments on Preferred Values

The preferred values of the absorption cross-sections, which are identical to those in our previous evaluation, IUPAC, 1997,[3] are taken from the work of Meller *et al.*[1] The cross-sections of Staffelbach *et al.*[2] agree to within 7% of those of Meller *et al.*[1] across the whole range of the two studies. The cross-sections obtained by Plum *et al.*[4] are approximately a factor of two lower than the values recommended here. It seems likely that the data of Plum *et al.*[4] were in error due to problems in handling the methylglyoxal.

Staffelbach *et al.*[2] also studied the cross-sections at three different temperatures, 248, 273, and 298 K. They found little variation in the cross-sections (≤10%) over this temperature range.

The preferred values for the quantum yields are taken from Staffelbach *et al.*[2] Raber and Moortgat[5] carried out methylglyoxal photolysis using two broad band radiation sources (275–380 nm and 390–470 nm) in synthetic air over a range of pressures (66 mbar–1 bar) and monitored the product yields by FTIR. The quantum yield of methylglyoxal photolysis was found to decrease with increasing pressure to give values at 1 bar of 0.64 and 0.23 with the shorter and longer wavelength lamps, respectively. The derivation of these values is based on modeling the substantial secondary chemistry in the system. Nevertheless, the values are clearly larger than those of Staffelbach *et al.*[2] Plum *et al.*[4] also found a higher value than Staffelbach *et al.*,[2] obtaining φ =0.11 with a source covering the range 290–470 nm, but this study made use of incorrect values of the absorption cross-sections. Even when the lower values of the quantum yields are used estimates of the photolysis rate of methylglyoxal in the atmosphere[4,5] suggest that photolysis may be the main process for its removal. More definitive measurements of the quantum yields are urgently required.

There is no direct information on the quantum yields of the individual photolysis channels. Both Staffelbach *et al.*[2] and Raber and Moortgat[5] are agreed that their results are best interpreted in terms of photolysis leading predominantly to $CH_3CO+HCO$ (channel 2). Staffelbach *et al.*[2] suggest that this is the only channel but Raber and Moortgat[5] conclude that the other two channels may contribute to an extent of ≤10% in their shorter wavelength studies.

References

[1] R. Meller, W. Raber, J. N. Crowley, M. E. Jenkin, and G. K. Moortgat, J. Photochem. Photobiol., A. **62**, 163 (1991).

[2] T. A. Staffelbach, J. J. Orlando, G. S. Tyndall, and J. G. Calvert, J. Geophys. Res. **100**, 14189 (1995).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

[4] C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., Environ. Sci. Technol. **17**, 479 (1983).

[5] W. H. Raber and G. K. Moortgat, "Photooxidation of Selected Carbonyl Compounds in Air: Methyl Ethyl Ketone, Methyl Vinyl Ketone, Methacrolein and Methylglyoxal," in *Progress and Problems in Atmospheric Chemistry*, edited by J. Barker (World Scientific, Singapore, 1997), Chap. 9.

$CH_3COCH_3 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3COCH_3 + h\nu \rightarrow CH_3CO + CH_3$	(1)	353.6	338
$\rightarrow 2CH_3 + CO$	(2)	399.5	299

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–355	Martinez *et al.*, 1992[1]	(a)
260–360	Hynes *et al.*, 1992[2]	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 = 0.76$	250	Meyrahn *et al.*, 1986[3]	(c)
$\phi_1 = 0.80$	260		
$\phi_1 = 0.64$	270		
$\phi_1 = 0.55$	280		
$\phi_1 = 0.30$	290		
$\phi_1 = 0.15$	300		
$\phi_1 = 0.05$	310		
$\phi_1 = 0.028$	320		
$\phi_1 = 0.033$	330		

Comments

(a) Cross-sections are the average cross-section over a 1 nm($\lambda > 280$ nm) or 4 nm($\lambda < 280$ nm) region centered at the corresponding wavelength (see Preferred Values).

(b) Cross-sections measured as a function of temperature over the range 260–360 K. Data were presented in graphical form and show a marked decrease in cross-section with decreasing temperature.

(c) Study of the quantum yield of formation of CO_2 and CO in the photolysis of dilute mixtures of acetone (0.13–0.20 mbar) in air (990 mbar) at room temperature. In addition, the quantum yields of formation of PAN were measured when trace amounts of NO_2(1.2×10^{-4} mbar) were added to the reactant mixtures. The listed values of ϕ_1 are the quantum yields of PAN, which were taken as a measure of the extent of primary process (1).

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$
202	0.533	295	3.52	330	0.067
206	0.125	296	3.35	331	0.051
210	0.104	297	3.20	332	0.040
214	0.120	298	3.07	333	0.031
218	0.163	299	2.91	334	0.026
222	0.242	300	2.77	335	0.017
226	0.361	301	2.66	336	0.014
230	0.533	302	2.53	337	0.011
234	0.774	303	2.37	338	0.009
238	1.086	304	2.24	339	0.006
242	1.479	305	2.11	340	0.005
246	1.944	306	1.952	341	0.005
250	2.47	307	1.801	342	0.003
254	3.04	308	1.663	343	0.004
258	3.61	309	1.537	344	0.002
262	4.15	310	1.408	345	0.002
266	4.58	311	1.276	346	0.001
270	4.91	312	1.173	347	0.002
274	5.06	313	1.081	348	0.001
278	5.07	314	0.967	349	0.001
280	5.05	315	0.858	350	0.001
281	5.01	316	0.777	351	0.000
282	4.94	317	0.699	352	0.001
283	4.86	318	0.608	353	0.000
284	4.76	319	0.530	354	0.001
285	4.68	320	0.467	355	0.000
286	4.58	321	0.407		
287	4.50	322	0.344		
288	4.41	323	0.287		
289	4.29	324	0.243		
290	4.19	325	0.205		
291	4.08	326	0.168		
292	3.94	327	0.135		
293	3.81	328	0.108		
294	3.67	329	0.086		

Quantum yields in air at 1 bar

λ/nm	ϕ_1
250	0.76
260	0.80
270	0.64
280	0.55
290	0.30
300	0.15
310	0.05
320	0.028
330	0.033

Comments on Preferred Values

The preferred absorption cross-sections are from the measurements of Martinez *et al.*[1] Over the wavelength region 260–320 nm these cross-sections are within 5% of our earlier recommendations based on the data of Calvert and Pitts[4] and Meyrahn *et al.*[3] The cross-sections reported by Hynes *et al.*[2] at room temperature contain large error limits at 320 and 340 nm but are in reasonable agreement with those recommended here.

This latter study[2] has also shown that the cross-sections are temperature dependent. Since no easily presentable formulation of the effect of temperature on the cross-sections was given, the original paper[2] should be consulted for details. It was noted, however, that neglecting the temperature dependence of the cross-sections results in significant overestimation of the photodissociation rates at lower temperature by, for example, ~50% at 220 K in the upper troposphere.[2]

The two studies[3,5] of the photodissociation of acetone in air are not in agreement regarding the quantum yield measurements. As pointed out by Meyrahn *et al.*,[3] further work on this system is needed to elucidate more quantitative details such as the collisional deactivation of photoexcited acetone. In the meantime, we have recommended the quantum yield data of Meyrahn *et al.*,[3] on the basis that the trend in ϕ_1 with wavelength observed by these authors appears to be reasonable.

The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[6]

References

[1] R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn, and J. A. Joens, Atmos. Environ. **26A**, 785 (1992).

[2] A. J. Hynes, E. A. Kenyon, A. J. Pounds, and P. H. Wine, Spectrochim. Acta **48A**, 1235 (1992).

[3] H. Meyrahn, J. Pauly, W. Schneider, and P. Warneck, J. Atmos. Chem. **4**, 277 (1986).

[4] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).

[5] E. P. Gardner, R. D. Wijayaratne, and J. G. Calvert, J. Phys. Chem. **88**, 5069 (1986).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3COC_2H_5 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CH_3COC_2H_5 + h\nu \rightarrow CH_3 + C_2H_5CO$	(1)	352.6	339
$\rightarrow C_2H_5 + CH_3CO$	(2)	349.4	342
$\rightarrow CH_3 + C_2H_5 + CO$	(3)	395.3	303

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–355	Martinez *et al.*, 1992[1]	(a)

Comments

(a) Conventional double-beam spectrophotometric measurements on mixtures of the ketone and argon at a resolution of 0.5 nm. The cross-sections are given as averages over a 1 nm ($\lambda > 280$ nm) or 4 nm($\lambda < 280$ nm) region centered on the corresponding wavelength (see Preferred Values).

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2
202	1.412	292	4.60	324	0.229
206	0.192	293	4.42	325	0.189
210	0.160	294	4.24	326	0.156
214	0.183	295	4.08	327	0.129
218	0.225	296	3.93	328	0.105
222	0.290	297	3.79	329	0.085
226	0.391	298	3.65	330	0.067
230	0.534	299	3.48	331	0.054
234	0.742	300	3.30	332	0.042
238	1.029	301	3.10	333	0.033
242	1.410	302	2.89	334	0.025
246	1.886	303	2.69	335	0.020
250	2.45	304	2.50	336	0.014
254	3.09	305	2.33	337	0.011
258	3.74	306	2.17	338	0.008
262	4.39	307	2.02	339	0.007
266	4.96	308	1.876	340	0.005
270	5.40	309	1.727	341	0.005
274	5.68	310	1.575	342	0.003
278	5.77	311	1.423	343	0.003
280	5.74	312	1.276	344	0.002
281	5.72	313	1.136	345	0.001
282	5.68	314	1.009	346	0.001
283	5.62	315	0.896	347	0.000
284	5.54	316	0.794	348	0.001
285	5.44	317	0.697	349	0.000
286	5.35	318	0.611	350	0.000
287	5.26	319	0.531	351	0.000
288	5.17	320	0.457	352	0.001
289	5.06	321	0.389	353	0.000
290	4.94	322	0.328	354	0.000
291	4.78	323	0.276	355	0.000

Comments on Preferred Values

The preferred absorption cross-sections are taken from the measurements of Martinez *et al.*[1] over the wavelength region 260–320 nm. These values are within 5% of those reported by Calvert and Pitts.[2] Raber and Moortgat[3] have also given a spectrum which is in good agreement with these cross-sections.

The only quantum yield measurements are those of Raber and Moortgat.[3] Methyl ethyl ketone was photolyzed in synthetic air at several pressures in the range 68 mbar–1 bar using a broad band radiation source (275–380 nm) and the product yields were monitored by FTIR. The quantum yield for photolysis of methyl ethyl ketone was found to be pressure dependent decreasing from 0.89 at 68 mbar to 0.34 at 1 bar. They also conclude that photolysis over the wavelength region used occurs to the extent of 80%–90% by channel (2). These results were derived by modeling the secondary chemistry in the system, which is substantial and we make no recommendation for the quantum yields until confirmatory studies are carried out.

References

[1] R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn, and J. A. Joens, Atmos. Environ. **26A**, 785 (1992).

[2] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).

[3] W. H. Raber and G. K. Moortgat, "Photooxidation of Selected Carbonyl Compounds in Air: Methyl Ethyl Ketone, Methyl Vinyl Ketone, Methacrolein and Methylglyoxal," in *Progress and Problems in Atmospheric Chemistry*, edited by J. Barker (World Scientific, Singapore, 1987), Chap. 9.

$CH_3OOH + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CH_3OOH + h\nu \rightarrow CH_3O + HO$	(1)	188	637
$\rightarrow CH_3 + HO_2$	(2)	292	410
$\rightarrow CH_3O_2 + H$	(3)	359	333

Absorption cross-section data

Wavelength range/nm	Reference	Comments
210–365	Vaghjiani and Ravishankara, 1989[1]	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 = 1.00 \pm 0.18$	248	Vaghjiani and Ravishankara, 1990[2]	(b)

Comments

(a) CH_3OOH prepared by methylation of H_2O_2 and shown by ^1H nuclear magnetic resonance (NMR) to be >97% pure (major impurity $C_2H_5OC_2H_5$). A diode-array spectrometer was used to make relative absorption measurements over the whole wavelength range and the results were put on an absolute basis by measurement of the cross sections at 213.9 nm (Zn line), and at 298.1, 326.1, 340.4, and 361.1 nm using Cd lines. The CH_3OOH concentration was determined by trapping the vapor at 77 K and titrating with Fe^{2+} or I^-.

(b) Direct measurement of products, HO by LIF, and $O(^3P)$ and H atoms by resonance fluorescence. Quantum yields for the formation of $O(^3P)$ and H atoms of <0.007 and 0.038 ± 0.007, respectively, were obtained.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\ \sigma/cm^2$	λ/nm	$10^{20}\ \sigma/cm^2$
210	31.2	290	0.691
215	20.9	295	0.551
220	15.4	300	0.413
225	12.2	305	0.313
230	9.62	310	0.239
235	7.61	315	0.182
240	6.05	320	0.137
245	4.88	325	0.105
250	3.98	330	0.079
255	3.23	335	0.061
260	2.56	340	0.047
265	2.11	345	0.035
270	1.70	350	0.027
275	1.39	355	0.021
280	1.09	360	0.016
285	0.863	365	0.012

Quantum Yields

$\phi_1 = 1.0$ for $\lambda > 290$ nm.

Comments on Preferred Values

The preferred absorption cross-section data are those of Vaghjiani and Ravishankara,[1] which are approximately 25% lower than the previously recommended data of Molina and Arguello.[3] The source of the discrepancy appears to lie in the determination of the concentrations of CH_3OOH in the absorption cell. Molina and Arguello[3] used a bubbler containing Fe^{2+} solution, which Vaghjiani and Ravishankara[1] showed does not give quantitative trapping.

On the basis of the results of Vaghjiani and Ravishankara,[2] who showed that $\phi_{OH} \sim 1.0$ at $\lambda = 248$ nm, we recommend that for atmospheric photolysis of CH_3OOH ϕ_1 be taken to be unity for wavelengths >290 nm.

The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

References

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

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

[3] M. J. Molina and G. Arguello, Geophys. Res. Lett. **6**, 953 (1979).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CH_3ONO_2 + h\nu \rightarrow CH_3O + NO_2$	(1)	170.1	703
$\rightarrow HCHO + HONO$	(2)	−68.4	
$\rightarrow CH_3ONO + O$	(3)	303.6	394

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–315	Roberts and Fajer, 1989[1]	(a)
220–335	Rattigan *et al.*, 1992[2]	(b)
236–344	Talukdar *et al.*, 1997[3]	(c)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 = 0.9 \pm 0.2$	248	Talukdar *et al.*, 1997[3]	(d)
$\phi_1 = 1.3 \pm 0.3$	248		(e)
$\phi_2 < 0.05$	248		(d)
$\phi_3 < 0.1$	248		(d)

Comments

(a) Absorption cross-sections were measured in a 10.2 cm pathlength cell, using a single-beam spectrometer with a photometric accuracy of ±0.5%. Numerical data for cross-sections are available from Ref. 4.

(b) Cross-sections were measured with a dual-beam diode array spectrometer with a spectral resolution of 0.3 nm over the temperature range 238–294 K. The temperature dependence of σ was found to obey the equation, $\ln \sigma(\lambda,T) = \ln \sigma(\lambda, 298\ \text{K}) + B(\lambda)(T-298)$.

(c) Absorption cross-sections were measured with a diode-array spectrometer. Absorbances were measured in 80 nm blocks which were assembled to construct the spectrum. Cross-sections were measured at 298 K and six other temperatures in the range 240–360 K. The temperature dependence of σ was found to obey the equation $\ln \sigma(\lambda,T) = \ln \sigma(\lambda, 298\ \text{K}) + B(\lambda)(T-298)$. The absorption cross-section at 213.86 nm (Zn line) was also measured. A value of $(1.67 \pm 0.08) \times 10^{-18}$ cm^2 molecule^{-1} was obtained.

(d) Photolysis of methyl nitrate at 248 nm and 298 K in the presence of excess O_2 to scavenge radicals. Actinometry based on O_3 photolysis or N_2O photolysis in experiments carried out with 193 nm radiation. Yields of the products CH_3ONO, CH_2O, NO_2, and NO_3 were measured by UVA, NO_3 by time-resolved absorption a 662 nm, and H and O by resonance fluorescence. Channels leading to H, O, and NO_3 were found to make negligible contribution at 248 nm, but high yields of C were obtained at 193 nm. Small yields of HO observed were attributed to secondary reactions.

(e) Same technique as in (d), but NO was used to scavenge radicals instead of O_2.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2
240	5.88	295	0.568
245	4.19	300	0.360
250	3.59	305	0.214
255	3.30	310	0.134
260	3.06	315	0.0633
265	2.77	320	0.0316
270	2.39	325	0.0144
275	2.00	330	0.00661
280	1.58	335	0.00274
285	1.19	340	0.00122
290	0.850		

Temperature dependence of the absorption cross-sections over the range 240–330 K[a]

λ/nm	$10^3\ B/K^{-1}$	λ/nm	$10^3\ B/K^{-1}$
240	3.48	290	4.04
245	3.29	295	4.47
250	2.96	300	4.94
255	2.82	305	5.56
260	2.83	310	6.33
265	2.92	315	7.34
270	3.08	320	8.74
275	3.28	325	9.97
280	3.51	330	13.6
285	3.78		

[a] The tabulated values of B may be used to calculate $\sigma(\lambda,T)$ using the relationship $\ln \sigma(\lambda,T)=\ln \sigma(\lambda,298\ \mathrm{K})+B(\lambda)(T-298)$.

Quantum Yields

$\phi_1=1.0$ for $\lambda \geq 248$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are average values from the data of Roberts and Fajer,[1] Rattigan *et al.*,[2] and Talukdar *et al.*,[3] which are in excellent agreement over the whole wavelength range of the measurements. They are also in reasonable agreement with the absorption spectrum reported by Calvert and Pitts[5] and with the cross-sections reported by Maria *et al.*[6] The results of Taylor *et al.*[7] are consistently higher than the values from the other studies,[1–3,5,6] by as much as a factor of two in the region 290–330 nm.

The two studies of the effect of temperature on the cross-sections are also in very good agreement with differences only appearing at wavelengths beyond 320 nm where the absorption cross-sections become very small and the precision of the measurements falls away. The preferred values of $B(\lambda)$ are those of Talukdar *et al.*[3] averaged over 5 nm intervals around the given wavelength.

The preferred value of the quantum yield is based on the work of Talukdar *et al.*[3] who concluded that the photodissociation of methyl nitrate at 248 nm produces NO_2 and CH_3O with a quantum yield essentially of unity. This is in accord with the general assumption[4] that the lack of structure in the absorption spectrum of $RONO_2$ molecules indicates that the quantum yield for dissociation is unity, and is supported by the recently measured value for ethyl nitrate of $\phi_1=1.0\pm0.1$ at 308 nm.[8]

References

[1] J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).

[2] O. Rattigan, E. Lutman, R. L. Jones, R. A. Cox, K. Clemitshaw, and J. Williams, J. Photochem. Photobiol. A **66**, 313 (1992); **69**, 125 (1992).

[3] R. K. Talukdar, J. B. Burkholder, M. Hunter, M. K. Giles, J. M. Roberts, and A. R. Ravishankara, J. Chem. Soc. Faraday Trans. **93**, 2797 (1997).

[4] J. M. Roberts, Atmos. Environ. **24A**, 243 (1990).

[5] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).

[6] H. J. Maria, J. R. McDonald, and S. P. McGlynn, J. Am. Chem. Soc. **95**, 1050 (1973).

[7] W. D. Taylor, T. D. Allston, M. J. Moscato, G. B. Fazekas, R. Kozlowski, and G. A. Takacs, Int. J. Chem. Kinet. **12**, 231 (1980).

[8] L. Zhu and C.-F. Ding, Chem. Phys. Lett. **265**, 177 (1997).

$C_2H_5ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H^\circ_{298}/\mathrm{kJ\cdot mol^{-1}}$	$\lambda_{\mathrm{threshold}}/\mathrm{nm}$
$C_2H_5ONO_2+h\nu \rightarrow C_2H_5O+NO_2$	(1)	171.7	697
$\rightarrow CH_3CHO+HONO$	(2)	−91.3	
$\rightarrow C_2H_5ONO+O$	(3)	299.4	400

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–315	Roberts and Fajer, 1989[1]	(a)
185–330	Turberg *et al.*, 1990[2]	(b)
265–340	Zhu and Ding, 1997[3]	(c)
235–340	Clemitshaw *et al.*, 1997[4]	(d)
236–340	Talukdar *et al.*, 1997[5]	(e)

Quantum yield data ($\phi=\phi_1+\phi_2+\phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1=1.0\pm0.1$	308	Zhu and Ding, 1997[3]	(f)

Comments

(a) Absorption cross-sections were measured in a 10.2 cm pathlength cell, using a single-beam spectrometer with a photometric accuracy of ±0.5%. Numerical data for cross-sections are available from Ref. 6.

(b) Absorption cross-sections were measured in cells of 2 and 10 cm pathlengths with a range of pressures of $C_2H_5ONO_2$. The spectral resolution was not specified.

(c) Cross-sections measured at 10 K intervals, between 238 and 298 K, using cavity ring-down spectroscopy. Absorption cross-sections were obtained by measuring optical loss as a function of sample gas pressure (0.013–18 mbar). The purity of ethyl nitrate was checked by FTIR and cavity ring-down spectroscopy.

(d) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm, over the temperature range 233–298 K. The purity of the ethyl nitrate was checked by NMR and FTIR.

(e) Absorption cross-sections were measured with a diode-array spectrometer at 298 K and six other temperatures in the range 240–360 K. Absorbances were measured in 80 nm blocks which were assembled to construct the spectrum. Corrections were made for contributions to the spectrum from NO_2 present in the ethyl nitrate.

(f) Excimer laser used to photodissociate ethyl nitrate in a cavity ring-down spectrometer. Time-resolved spectra of products observed. Only NO_2 found as product, with undetectable yields of HONO and C_2H_5ONO. Quantum yield measurements were made at 278, 283, 288, 293. and 298 K with ethyl nitrate pressures of 1.3–13 mbar in a buffer gas of N_2 at total pressures of 16 mbar to 1 bar. ϕ_1 was found to be pressure and temperature independent.

Preferred Values

Absorption cross-sections at 298 K and their temperature dependence over the ranges 233–360 K and 235–340 nm[a]

λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	$10^3\ B/\mathrm{K}^{-1}$	λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	$10^3\ B/\mathrm{K}^{-1}$
185	1710		265	3.6	2.9
190	1710		270	3.1	3.1
195	1490		275	2.7	3.3
200	1140		280	2.2	3.6
205	738		285	1.7	3.8
210	400		290	1.2	4.2
215	195		295	0.85	4.7
220	91		300	0.55	5.1
225	45		305	0.33	5.8
230	24		310	0.19	6.7
235	11.9	1.4	315	0.10	7.9
240	7.7	2.8	320	0.051	8.6
245	5.4	2.9	325	0.026	10.4
250	4.5	2.8	330	0.012	12.9
255	4.1	2.6	335	0.0049	14.1
260	3.9	2.6	340	0.0025	15.6

[a] The temperature variation of the absorption cross-section at a particular wavelength in the range 240–340 nm is expressed as $\ln\sigma(T)-\ln\sigma(298\ \mathrm{K})=B(T-298)$.

Quantum Yields

$\phi_1=1.0\pm0.1$ at 308 nm, independent of pressure over the temperature range 278–298 K.

Comments on Preferred Values

Since our previous evaluation, IUPAC, 1997,[7] there have been three new studies[3–5] of the absorption cross-sections and their temperature dependence. The new results at 298 K are in excellent agreement with the previous two studies[1,2] on which the recommendation in IUPAC, 1997[7] were based. The preferred values of the cross-sections at 298 K are those obtained by Turberg *et al.*[2] over the range 185–230 nm, where this is the only study, and for the range 235–340 nm averages are taken of the values from all of the five studies[1–5] at the wavelengths where they overlap. The resulting values are within a few percent of the preferred values recommended in our previous evaluation, IUPAC, 1997.[7]

The temperature variation of the cross-sections has also been studied by Zhu and Ding,[3] Clemitshaw *et al.*,[4] and Talukdar *et al.*[5] These studies together cover the temperature range 233–360 K and the wavelength range 235–340 nm. It is found in all of the studies that the temperature variation of σ can be expressed as $\ln\sigma(\lambda,T)-\ln\sigma(\lambda,298\ \mathrm{K})=B(\lambda)(T-298)$. The results from the three studies[3–5] are in good agreement and the preferred values of B have been obtained by averaging values from the three studies.[3–5]

The only direct measurement of the quantum yield is that of Zhu and Ding.[3] Their finding that at 308 nm the sole photodissociation channel is that leading to NO_2 production with a quantum yield of unity is accepted for our preferred value of the quantum yield. It is in accord with the studies of Luke *et al.*[8,9] who concluded that the measured rates of NO_2 production from ethyl nitrate photolysis in sunlight could be accounted for by assuming that $\phi_1 = 1$ throughout the region 290–340 nm. This is also supported by the recently measured value of unity for the same channel in the 248 nm photolysis of methyl nitrate.[5]

References

[1] J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).

[2] M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P. Klingensmith, and G. A. Takacs, J. Photochem. Photobiol. **A51**, 281 (1990).

[3] L. Zhu and C.-F. Ding, Chem. Phys. Lett. **265**, 177 (1997).

[4] K. C. Clemitshaw, J. Williams, O. V. Rattigan, D. E. Shallcross, K. S. Law, and R. A. Cox, J. Photochem. Photobiol. A. **102**, 117 (1997).

[5] R. K. Talukdar, J. B. Burkholder, M. Hunter, M. K. Giles, J. M. Roberts, and A. R. Ravishankara, J. Chem. Soc. Faraday Trans. **93**, 2797 (1997).

[6] J. M. Roberts, Atmos. Environ. **24A**, 243 (1990).

[7] IUPAC, Supplement V, 1997 (see references in Introduction).

[8] W. T. Luke and R. R. Dickerson, Geophys. Res. Lett. **15**, 1181 (1988).

[9] W. T. Luke, R. R. Dickerson, and L. J. Nunnermacker, J. Geophys. Res. **94**, 14905 (1989).

$n\text{-}C_3H_7ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$n\text{-}C_3H_7ONO_2 + h\nu \rightarrow n\text{-}C_3H_7O + NO_2$	(1)	165.9	721
$\rightarrow C_2H_5CHO + HONO$	(2)	−92.8	
$\rightarrow C_3H_7ONO + O$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–330	Roberts and Fajer, 1989[1]	(a)
185–330	Turberg *et al.*, 1990[2]	(b)
220–340	Clemitshaw *et al.*, 1997[3]	(c)

Comments

(a) Absorption cross-sections were measured in a cell of 10.2 cm pathlength using a single-beam spectrometer with a photometric accuracy of ±0.5%. No NO_2 could be detected by FTIR in the *n*-propyl nitrate.

(b) Absorption cross-sections were measured in 2 and 10 cm pathlength cells with a range of pressures of $n\text{-}C_3H_7ONO_2$ at an unspecified spectral resolution.

(c) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm. The purity of the *n*-propyl nitrate was checked by NMR and FTIR.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\ \sigma/\text{cm}^2$	λ/nm	$10^{20}\ \sigma/\text{cm}^2$
185	1810	265	3.6
190	1800	270	3.2
195	1600	275	2.8
200	1260	280	2.3
205	855	285	1.8
210	489	290	1.3
215	244	295	0.95
220	105	300	0.57
225	50	305	0.34
230	27	310	0.19
235	15	315	0.10
240	8.9	320	0.053
245	6.0	325	0.031
250	4.8	330	0.022
255	4.4	335	0.018
260	4.0	340	0.016

Comments on Preferred Values

Since our previous evaluation, IUPAC, 1997,[4] Clemitshaw *et al.*[3] have measured the absorption cross-sections at 298 K over the range 220–340 nm. In the wavelength region where their measurements overlap with those of Roberts and Fajer[1] (270–320 nm), the two studies are in excellent agreement. Agreement with the results of Turberg *et al.*[2] is also very good in the range 220–295 nm, but the results of Turberg *et al.*[2] deviate significantly from those of both Clemitshaw *et al.*[3] and Roberts and Fajer[1] at $\lambda > 295$ nm. This tendency to obtain higher values of the absorption cross-section at longer wavelengths is noticeable in the results of Turberg *et al.*[2] in all of their studies of the higher nitrates and could be due to traces of NO_2 in their samples.

The preferred values of the absorption cross-section are those of Turberg *et al.*[2] for the range 185–220 nm where theirs are the only measurements. Over the range 220–295 nm averages are taken of the results of Roberts and Fajer,[1] Turberg *et al.*,[2] and Clemitshaw *et al.*[3] where their studies overlap, and over the range 295–340 nm the preferred values are based on the results of Roberts and Fajer[1] and Clemitshaw *et al.*[3]

There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for photodissociation of both ethyl and methyl nitrate to form NO_2 have been shown to be unity at 308 and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of organic nitrates are very similar, with structureless continua occurring in the same region of the spectrum, it seems likely that the photodissociation quantum yield for *n*-propyl nitrate will also be unity. Further support for this conclusion comes from direct measurements[5] of the rate of formation of NO_2 from the photolyses of $n\text{-}C_3H_7ONO_2$ in sunlight. These agreed well with the calculated rates of photolyses, based on measurements of the absorption cross sections, solar irradiances, and an assumed value of $\phi_1 = 1$ throughout the wavelength region 290–340 nm.[5]

References

[1] J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).

[2] M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P. Klingensmith, and G. A. Takacs, J. Photochem. Photobiol. **A51**, 281 (1990).

[3] K. C. Clemitshaw, J. Williams, O. V. Rattigan, D. E. Shallcross, K. S. Law, and R. A. Cox, J. Photochem. Photobiol. A **102**, 117 (1997).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

[5] W. T. Luke, R. R. Dickerson, and L. J. Nunnermacker, J. Geophys. Res. **94**, 14905 (1989).

$i\text{-}C_3H_7ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$i\text{-}C_3H_7ONO_2 + h\nu \rightarrow 2\text{-}C_3H_7O + NO_2$	(1)	171.7	697
$\rightarrow CH_3COCH_3 + HONO$	(2)	−105.9	
$\rightarrow i\text{-}C_3H_7ONO + O$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–330	Roberts and Fajer, 1989[1]	(a)
185–330	Turberg *et al.*, 1990[2]	(b)
220–340	Clemitshaw *et al.*, 1997[3]	(c)
240–360	Talukdar *et al.*, 1997[4]	(d)

Comments

(a) Absorption cross-sections were measured in a 10.2 cm pathlength cell using a single-beam spectrophotometer with a photometric accuracy of ±0.5%. Numerical data for cross-sections are available from Ref. 5. Samples were checked by FTIR for the presence of NO_2, which was not found.

(b) Absorption cross-sections were measured in 2 and 10 cm pathlength cells, with a range of pressures of $i\text{-}C_3H_7ONO_2$, at a bandwidth of 1 nm.

(c) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm. The purity of the *i*-propyl nitrate was checked by NMR and FTIR.

(d) Absorption cross-sections were measured with a diode-array spectrometer at 298 K and six other temperatures in the range 240–360 K. Absorbances were measured in 80 nm blocks which were assembled to construct the spectrum.

Preferred Values

Absorption cross-sections at 298 K and their temperature dependence over the ranges 233–360 K and 240–340 nm[a]

λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	$10^3\ B/\mathrm{K}^{-1}$	λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	$10^3\ B/\mathrm{K}^{-1}$
185	1790		275	3.4	3.3
188	1810		280	2.8	3.6
190	1790		285	2.2	4.0
195	1610		290	1.6	4.4
200	1260		295	1.2	4.8
205	867		300	0.78	5.4
210	498		305	0.50	6.1
215	247		310	0.29	6.9
220	125		315	0.17	8.1
225	62		320	0.085	9.4
230	34		325	0.044	11.1
235	18		330	0.022	11.9
240	11	2.8	335	0.011	14.0
245	7.0	2.7	340	0.0053	13.9
250	5.4	2.5	345	0.0018	
255	4.9	2.5	350	0.00080	
260	4.6	2.6	355	0.00029	
265	4.3	2.8	360	0.00018	
270	3.9	3.1			

[a] The temperature variation of the absorption cross-section at a particular wavelength in the range 240–340 nm is expressed as $\ln \sigma(T) - \ln \sigma(298\ \mathrm{K}) = B(T-298)$.

Comments on Preferred Values

Since our previous evaluation, IUPAC, 1997,[6] Clemitshaw *et al.*[3] have measured the absorption cross-sections at 298 K over the range 220–340 nm and Talukdar *et al.*[4] have measured both the cross-sections at 298 K over the range 240–360 nm and their temperature dependence at temperatures in the range 240–360 K. The results of Clemitshaw *et al.*[3] and of Talukdar *et al.*[4] are in excellent agreement with the earlier results of Roberts and Fajer[1] and Turberg *et al.*[2] at wavelengths where they overlap (in the range 220–330 nm), except for the results of Turberg *et al.*[2] at wavelengths ≥310 nm which deviate increasingly from those of the other studies as the wavelength increases. This tendency, to obtain higher values than others in this wavelength region, is noticeable in the results of Turberg *et al.*[2] for all of the higher nitrates and could be due to traces of NO_2 present in their samples.

The preferred values of the absorption cross-sections at 298 K are those of Turberg *et al.*[2] for the range 185–220 nm, where theirs are the only values. Over the range 220–305 nm averages are taken of the results of Roberts and Fajer,[1] Turberg *et al.*,[2] Clemitshaw *et al.*,[3] and Talukdar *et al.*,[4] where their studies overlap, and over the range 310–360 nm the preferred values are based on the results of Roberts and Fajer,[1] Clemitshaw *et al.*,[3] and Talukdar *et al.*[4]

The preferred values of the constant *B*, which characterize the temperature dependence of the absorption cross-sections are those of Talukdar *et al.*[4]

There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for the photodissociation of both ethyl and methyl nitrate to form NO_2 have been shown to be unity at 308 and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of organic nitrates are very similar structureless continua occurring at similar wavelengths, it seems likely that the photodissociation quantum yield for isopropyl nitrate will also be unity. Further support for this conclusion comes from measurements of the rate of formation of NO_2 from the photolyses of alkyl nitrates in sunlight.[7] Thus the measured rate of formation of NO_2 matched well with calculated rates of photolyses based on measurements of the absorption cross section, solar irradiances, and an assumed value of $\phi_1 = 1$ throughout the wavelength region 290–330 nm.[7]

References

[1] J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).

[2] M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P. Klingensmith, and G. A. Takacs, J. Photochem. Photobiol. **A51**, 281 (1990).

[3] K. C. Clemitshaw, J. Williams, O. V. Rattigan, D. E. Shallcross, K. S. Law, and R. A. Cox, J. Photochem. Photobiol. A. **102**, 117 (1997).

[4] R. K. Talukdar, J. B. Burkholder, M. Hunter, M. K. Giles, J. M. Roberts, and A. R. Ravishankara, J. Chem. Soc. Faraday Trans. **93**, 2797 (1997).

[5] J. M. Roberts, Atmos. Environ. **24A**, 243 (1990).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

[7] W. T. Luke, R. R. Dickerson, and L. J. Nunnermacker, J. Geophys. Res. **94**, 14905 (1989).

$1\text{-}C_4H_9ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H^\circ_{298}/\mathrm{kJ \cdot mol^{-1}}$	$\lambda_{\mathrm{threshold}}/\mathrm{nm}$
$1\text{-}C_4H_9ONO_2 + h\nu \rightarrow 1\text{-}C_4H_9O + NO_2$	(1)		
$\rightarrow 1\text{-}C_3H_7CHO + HONO$	(2)		
$\rightarrow 1\text{-}C_4H_9ONO + O$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–315	Roberts and Fajer, 1989[1]	(a)
185–320	Turberg *et al.*, 1990[2]	(b)
220–340	Clemitshaw *et al.*, 1997[3]	(c)

Comments

(a) Absorption cross-sections were measured in a 10.2 cm pathlength cell using a single-beam spectrophotometer with a photometric accuracy of ±0.5%. Data are presented graphically but an expression for σ as a function of λ is derived from a least-squares fit to the data at $\lambda \geqslant 270$ nm. Purity of the butyl nitrate was checked by FTIR.

(b) Absorption cross-sections were measured in 2 and 10 cm pathlength cells in a Varian Carey 219 spectrophotometer using a bandwidth of 1 nm.

(c) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm. The purity of the ethyl nitrate was checked by NMR and FTIR.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\ \sigma/\text{cm}^2$	λ/nm	$10^{20}\ \sigma/\text{cm}^2$
185	1810	265	3.9
190	1810	270	3.4
195	1620	275	3.0
200	1300	280	2.4
205	889	285	1.9
210	518	290	1.4
215	263	295	0.89
220	111	300	0.57
225	58	305	0.34
230	30	310	0.19
235	17	315	0.10
240	9.8	320	0.051
245	6.3	325	0.031
250	5.3	330	0.021
255	4.6	335	0.016
260	4.3	340	0.013

Comments on Preferred Values

The results of Roberts and Fajer,[1] Turberg *et al.*,[2] and Clemitshaw *et al.*[3] are in good agreement at wavelengths where the studies overlap (in the range 220–320 nm), except for the results of Turberg *et al.*[2] at wavelengths ⩾300 nm which deviate increasingly from those of the other studies as the wavelength increases. This tendency to obtain higher values than others in this wavelength region, is noticeable in the results of Turberg *et al.*[2] for all of the higher nitrates and could be due to traces of NO_2 present in their samples.

The preferred values of the absorption cross-sections are those of Turberg *et al.*,[2] for the range 185–220 nm, where theirs are the only values. Over the range 220–295 nm averages are taken of the results of Roberts and Fajer,[1] Turberg *et al.*,[2] and Clemitshaw *et al.*,[3] where their studies overlap, and over the range 300–400 nm the preferred values are based on the results of Roberts and Fajer[1] and Clemitshaw *et al.*[3]

There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for the photodissociation of both ethyl and methyl nitrates to form NO_2 have been shown to be unity at 308 and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of alkyl nitrates are very similar structureless continua occurring at similar wavelengths, it seems likely that the photodissociation quantum yield for 1-butyl nitrate will also be unity. Further support for this conclusion comes from measurements of the rate of formation of NO_2 from the photolyses of alkyl nitrates in sunlight.[4] Thus the measured rate of formation of NO_2 matched well with calculated rates of photolyses based on measurements of the absorption cross sections, solar irradiances, and an assumed value of $\phi_1 = 1$ throughout the wavelength region 290–330 nm.[4]

References

[1] J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).

[2] M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P. Klingensmith, and G. A. Takacs, J. Photochem. Photobiol. **A51**, 281 (1990).

[3] K. C. Clemitshaw, J. Williams, O. V. Rattigan, D. E. Shallcross, K. S. Law, and R. A. Cox, J. Photochem. Photobiol. A. **102**, 117 (1997).

[4] W. T. Luke, R. R. Dickerson, and L. J. Nunnermacker, J. Geophys. Res. **94**, 14905 (1989).

$2\text{-}C_4H_9ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$2\text{-}C_4H_9ONO_2 + h\nu \rightarrow 2\text{-}C_4H_9O + NO_2$	(1)		
$\rightarrow CH_3COC_2H_5 + HONO$	(2)		
$\rightarrow 2\text{-}C_4H_9ONO + O$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
250–320	Roberts and Fajer, 1989[1]	(a)

Comments

(a) Absorption cross-sections were measured in a cell of 10.2 cm pathlength using a single-beam spectrophotometer with a photometric accuracy of ±0.5%. The expression for σ as a function of λ was derived from a least-squares fit to the data at $\lambda \geq 270$ nm.

Preferred Values

Absorption cross-sections at 298 K[a,b]

λ/nm	$10^{20}\ \sigma/\text{cm}^2$	λ/nm	$10^{20}\ \sigma/\text{cm}^2$
250	6.5	290	1.8
255	5.6	295	1.3
260	5.2	300	0.74
265	4.8	305	0.50
270	4.2	310	0.29
275	3.7	315	0.15
280	3.1	320	0.08
285	2.4		

[a] Values at $\lambda \leq 265$ nm are taken from graphs in Ref. 1.
[b] Values at $\lambda \geq 270$ nm are calculated from the expression given in Ref. 1 based on a least-squares fit to the data.

Comments on Preferred Values

The only available measurements of the absorption cross-sections are those of Roberts and Fajer.[1] Their measurements of cross-sections for other alkyl nitrates have agreed well with other studies, and their values are accepted as the preferred values for 2-butyl nitrate.

There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for the photodissociation of both ethyl and methyl nitrates to form NO_2 have been shown to be unity at 308 and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of alkyl nitrates are very similar structureless continua occurring at similar wavelengths, it seems likely that the photodissociation quantum yield for 2-butyl nitrate will also be unity. Further support for this conclusion comes from measurements of the rate of formation of NO_2 from the photolyses of alkyl nitrates in sunlight.[2] Thus the measured rate of formation of NO_2 matched well with the calculated rates of photolyses based on measurement of the absorption cross sections, solar irradiances, and an assumed value of $\phi = 1$ throughout the wavelength region 290–330 nm.[2]

References

[1] J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).
[2] W. T. Luke, R. R. Dickinson, and L. J. Nunnermacker, J. Geophys. Res. **94**, 14905 (1989).

$CH_3O_2NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1} [a]	$\lambda_{threshold}$/nm
$CH_3O_2NO_2 + h\nu \rightarrow CH_3O_2 + NO_2$	(1)	88	1359
$\rightarrow CH_3O + NO_3$	(2)	135	886

[a] Only approximate values of ΔH°_{298} values are given since the heat of formation of $CH_3O_2NO_2$ is not well known.

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–280	Bridier, Lesclaux, and Veyret, 1992[1]	(a)

Comments

(a) Flash photolysis of Cl_2 in the presence of CH_4–O_2–NO_2 mixtures at a total pressure of 1 bar, with UV absorption to monitor the concentrations of CH_3O_2 radicals and $CH_3O_2NO_2$.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	500	265	20.0
205	360	270	16.0
210	240	275	13.0
215	150	280	10.5
220	105	285	6.2
225	80	290	3.9
230	68	295	2.4
235	60	300	1.4
240	53	305	0.85
245	46	310	0.53
250	39	315	0.39
255	32	320	0.24
260	26	325	0.15

Comments on Preferred Values

In view of the thermal instability of $CH_3O_2NO_2$, the measurement of the cross-sections for $CH_3O_2NO_2$ presents considerable experimental problems. Nevertheless, the measurements of Bridier *et al.*[1] are in moderately good agreement with previous data[2–4] at wavelengths <255 nm and are taken as the preferred values in the range 200–280 nm. At longer wavelengths the agreement is less good and the experimental data from Cox and Tyndall,[2] which are the only values extending into the wavelength region of importance for the troposphere (λ≥290 nm), show large scatter. The preferred values given in the table for wavelengths >280 nm are based on a comparison with the spectrum of HO_2NO_2 (IUPAC, 1997[5]). The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[6]

There are no data to indicate the relative importance of the two photodissociation channels, and neither can be precluded on energetic grounds in the absorbing wavelength region. By analogy with other molecules containing the $-NO_2$ chromophore (for example, HNO_3), it is likely that absorption around 270 nm is associated with an orbitally forbidden $n-\pi^*$ transition which leads to dissociation of the molecule. Thus it is probable that $\phi_1 + \phi_2 = 1$.

References

[1] I. Bridier, R. Lesclaux, and B. Veyret, Chem. Phys. Lett. **191**, 259 (1992).
[2] R. A. Cox and G. S. Tyndall, Chem. Phys. Lett. **65**, 357 (1979).
[3] O. Morel, R. Simonaitis, and J. Heicklen, Chem. Phys. Lett. **73**, 38 (1980).
[4] S. P. Sander and R. T. Watson. J. Phys. Chem. **84**. 1664 (1980).
[5] IUPAC, Supplement VI, 1997 (see references in Introduction).
[6] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3C(O)OONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CO_3NO_2 + h\nu \rightarrow CH_3CO_3 + NO_2$	(1)	119	1005
$\rightarrow CH_3CO_2 + NO_3$	(2)	124	965

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–325	Libuda and Zabel, 1995[1]	(a)
196–350	Talukdar *et al.*, 1995[2]	(b)

Quantum yield data ($\phi = \phi_1 + \phi_1$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi(NO_2)$	248	Mazely, Friedl, and Sander, 1995[3]	(c)

Comments

(a) Longpath (39.1 m) UV absorption cell with diode array detector used. The concentration of the $CH_3C(O)OONO_2$ was determined by FTIR (pathlength, 51.6 m) in the same cell. The UV spectral resolution was 0.6 nm.

(b) Diode array spectrometer with a resolution of 0.2 nm used with temperature controlled (±1 K) absorption cells of pathlengths 100 and 25 cm. $CH_3C(O)OONO_2$ concentrations were determined by pressure measurements. Cross-sections were measured at 250, 273, and 298 K.

(c) Pulsed laser photolysis of PAN with LIF detection of NO_2. The quantum yield for NO_2 formation was measured relative to that from the photodissociation of HNO_3 at 248 nm, assuming a value of $\phi(NO_2)$ from HNO_3 of unity at this wavelength (see data sheet for HNO_3 photolysis, IUPAC, 1997[4]). A value of $\phi(NO_2) = 0.83 \pm 0.09$ for the photolysis of PAN at 248 nm was obtained.

Preferred Values

Absorption cross-sections at 298 K and the temperature coefficient B[a]

λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	$10^3\ B/\mathrm{K}^{-1}$	λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	$10^3\ B/\mathrm{K}^{-1}$
196	429	2.02	274	2.45	5.55
198	398	1.73	276	2.07	5.76
200	361	1.36	278	1.74	5.98
202	325	1.07	280	1.46	6.20
204	292	0.86	282	1.21	6.43
206	261	0.75	284	1.01	6.67
208	226	0.71	286	0.81	6.90
210	196	0.75	288	0.648	7.15
212	168	0.84	290	0.537	7.39
214	143	0.97	292	0.447	7.63
216	122	1.12	294	0.369	7.86
218	104	1.29	296	0.297	8.08
220	89.7	1.47	298	0.245	8.27
222	77.7	1.64	300	0.189	8.44
224	67.6	1.81	302	0.152	8.61
226	59.3	1.98	304	0.125	8.76
228	52.0	2.14	306	0.0998	8.87
230	45.8	2.30	308	0.0816	9.01
232	40.4	2.46	310	0.0666	9.13
234	35.5	2.63	312	0.0538	9.30
236	31.4	2.80	314	0.0462	9.46
238	27.9	2.96	316	0.0363	9.57
240	24.4	3.11	318	0.0300	9.75
242	21.5	3.25	320	0.0252	10.0
244	18.8	3.39	322	0.0199	10.2
246	16.6	3.52	324	0.0166	10.4
248	14.6	3.64	326	0.0140	10.6
250	12.9	3.76	328	0.0117	10.7
252	11.4	3.87	330	0.0106	10.9
254	10.0	3.98	332	0.00857	11.2
256	8.86	4.10	334	0.00676	11.5
258	7.8	4.23	336	0.00615	11.7
260	6.85	4.38	338	0.00526	11.9
262	6.01	4.53	340	0.00502	12.2
264	5.23	4.68	342	0.00360	12.4
266	4.54	4.82	344	0.00241	12.5
268	3.94	4.97	346	0.00231	-
270	3.37	5.14	348	0.00247	-
272	2.87	5.34	350	0.00165	-

[a] Absorption cross-sections at temperatures in the range 250–298 K are calculated using the equation $\ln[\sigma(T)/\sigma(298\ \mathrm{K})]=B(T-298)$.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are based on the work of Libuda and Zabel[1] and Talukdar *et al.*,[2] which agree to within a few percent at wavelengths below 290 nm and only slightly less well at longer wavelengths where the error limits on the measurements increase because of the difficulty of measuring the small cross-sections in that region of the spectrum. The preferred values at 298 K differ significantly from those in our previous evaluation, IUPAC, 1997,[5] particularly at longer wavelengths.

Talukdar *et al.*[2] have also measured the cross-sections at three temperatures and expressed their results in the form $\ln[\sigma(T)/\sigma(298\ \mathrm{K})]=B(T-298)$ where B is a constant at a particular wavelength. The values of B and $\sigma(298\ \mathrm{K})$ obtained by Talukdar *et al.*[2] are listed as our preferred values.

Measurements are still needed on the quantum yields and relative importance of the proposed primary processes as a function of wavelength. The NO_2 formation quantum yield measured by Mazely *et al.*[3] at 248 nm suggests that pathway (1) dominates. It is therefore suggested that $(\phi_1+\phi_2)=1$ for absorption in the UV region and that channel (1) forming $CH_3C(O)O_2$ and NO_2 is the dominant photochemical primary process.

References

[1] H. G. Libuda and F. Zabel, Ber. Bunsenges. Phys. Chem. **99**, 1205 (1995).

[2] R. A. Talukdar, J. B. Burkholder, A.-M. Schmolter, J. M. Roberts, R. R. Wilson, and A. R. Ravishankara, J. Geophys. Res. **100**, 14163 (1995).

[3] T. L. Mazely, R. R. Friedl, and S. P. Sander, J. Phys. Chem. **99**, 8162 (1995).

[4] IUPAC, Supplement VI, 1997 (see references in Introduction).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

5. Appendix 1

Enthalpy Data*

Species	$\Delta_f H^\circ_{298}/\mathrm{kJ \cdot mol^{-1}}$	$\Delta_f H^\circ_0/\mathrm{kJ \cdot mol^{-1}}$	Reference
H	217.998±0.006	216.03±0.006	27
H_2	0	0	27
$O(^3P)$	249.18±0.10	246.79±0.10	27
$O(^1D)$	438.9	436.6	32
O_2	0	0	27
$O_2(^1\Delta)$	94.3	94.3	32
$O_2(^1\Sigma)$	156.9	156.9	32
O_3	142.7	145.35	67
HO	39.3±2.1	39.0±2.1	40
HO_2	14.6		40
H_2O	−241.826±0.040	−238.92±0.04	27
H_2O_2	−136.31	−130.04	67
N	472.68±0.40		27
N_2	0	0	27
NH	352±10		58
NH_2	188.7±1.3		40
NH_3	−45.94±0.35		27
NO	90.25	89.75	67
NO_2	33.18	35.98	67
NO_3	73.72±1.4	78.95±1.4	28
N_2O	82.05	85.500	67
N_2O_4	9.1±1.7	18.7±1.7	21
N_2O_5	11.3		21,28
HNO	112.95±0.25	110.02±0.25	31
HNO_2	−79.5		67
HNO_3	−135.06	−125.27	67
HO_2NO_2	−57.24		56
CH	596.4±1.2		40
$CH_2(^3B_1)$	390.4±4		40
$CH_2(^1A_1)$	428.3±4		40
CH_3	146.4±0.4		40
CH_4	−74.81	−66.818	67
CN	435±10		21,40
HCN	135±8		21
HCO	43.1		6,23
CH_2O	−108.6	−104.7	32
CH_3O	17.2±3.8		40
CH_2OH	−17.8±1.3	−11.5±1.3	39
CH_3OH	−201.6±0.2		26
CO	−110.53±0.17		27
NCO	159±10		21
HOCO		−205±10	35
COOH	−223.0		40
HCOOH	−378.8±0.5	−371.6	26
CH_3O_2	10.4±3.1		46
CH_3OOH	−131		9
$HOCH_2O_2$	−162.1±2.1		46
CH_3ONO	−65.3		9
CH_3ONO_2	−119.7		9
$CH_3O_2NO_2$	−44		56
CO_2	−393.51±0.13		27
C_2H	566.1±2.9		40
C_2H_2	228.0±1.0		26
C_2H_3	300.0±3.4		40
C_2H_4	52.2±1.2		26
C_2H_5	120.9±1.6		40
C_2H_6	−84.0±0.2		26
CH_2CN	243.1±11.3		40
CH_3CN	64.3±26.3		61
CH_2CO	−47.7±1.6		55
CH_3CO	−10.0±1.2		40
CH_2CHO	10.5±9.2		40
$CH{=}CHOH$		120±10	34
CH_3CHO	−165.8±0.4		26,61
C_2H_5O	−15.5±3.4		40
C_2H_4OH		−23±6	34
CH_3CHOH	−63.6±4.2		40
C_2H_5OH	−234.8±0.2		26,61
$(CHO)_2$	−211.9±0.8		26,61
CH_3CO_2	−207.5±4		40
CH_3CO_2H	−432.14±0.4		26,61
$C_2H_5O_2$	−28.7±6.5		46
CH_3OOCH_3	−125.7±1.3		26,61
$CH_3C(O)O_2$	−172±20		46
C_2H_5ONO	−103.8		26,61
$C_2H_5ONO_2$	−154.1±1.0		26,61
$C_2H_5O_2NO_2$	−63.2		30
$CH_3C(O)O_2NO_2$	−258±22		14
$CH_2{=}CHCH_2$	170.7±8.8		40
C_3H_6	20.2±0.4		26,61
$n\text{-}C_3H_7$	97.5±2.5		40
$i\text{-}C_3H_7$	90.0±1.6		40
C_3H_8	−104.5±0.3		26,61
C_2H_5CO	−32.3±4.2		10,68
CH_3COCH_2	−23.9±10.9		40
C_2H_5CHO	−187.4±1.5		26,61
CH_3COCH_3	−217.2±0.4		26,61
C_3H_6OH	−74		9
$n\text{-}C_3H_7O$	−41.4		40
$i\text{-}C_3H_7O$	−52.3		40
$i\text{-}C_3H_7OH$	−272.5±0.4		26,61
CH_3COCHO	−271.1±4.7		26,61
$C_3H_5O_2$	87.9±5.5		46
$i\text{-}C_3H_7O_2$	−68.9±5.1		46
$n\text{-}C_3H_7ONO_2$	−174.1±1.3		26,61
$i\text{-}C_3H_7ONO_2$	−190.8±1.7		26,61
$n\text{-}C_4H_9$	76.3±5.0		16
$s\text{-}C_4H_9$	67.4±2.1		40
$n\text{-}C_4H_{10}$	−125.7±0.4		26
$n\text{-}C_3H_7CHO$	−204.8±1.5		26
$CH_3COC_2H_5$	−238.5±0.5		26
$n\text{-}C_4H_9O$	−62.8		40
$s\text{-}C_4H_9O$	−69.5±3.3		40
S	277.17±0.15		27
HS	143.01±2.85	142.55±3.01	53
H_2S	−20.6±0.5		27
HSO	−4		47
SO	5.0±1.3	5.0±1.3	21
HSO_2	−222		13
SO_2	−296.81±0.20		27
$HOSO_2$	−385		48
SO_3	−395.72	−389.99	67
HSNO	94		12
CH_3S	124.60±1.84		53
CH_3SH	−22.9±0.6		57
CH_3SCH_2	136.8±5.9		37
CH_3SCH_3	−37.24	−21.058	67
CS	272	268	8
CH_3SO	−67±10		17
CH_3SOO	75.7±4.2	87.9±4.6	65
OCS	−142.09	−142.218	67

Enthalpy Data*—Continued

Species	$\Delta_f H^\circ_{298}$/kJ·mol^{-1}	$\Delta_f H^\circ_0$/kJ·mol^{-1}	Reference
S_2	128.60		27
CH_3SS	72.4±4.2		8
CH_3SSCH_3	−24.3		8
CS_2	117.36	116.57	67
$HOCS_2$	110.5±4.6		50
F	79.38±0.30		27
HF	−273.30±0.70		27
HOF	−98.3±4.2	−95.4±4.2	21
FO	109±10	108±10	20
FO_2	25.4±2	27.2±2	20
FONO	67		4
FNO_2	−108.8		56
$FONO_2$	10	18	21
CH_2F	−31.8±8.4		40
CH_3F	−232.6		42
CH_3CH_2F	−263±2		45
HCOF		−392.5±6.3	69
FCO	−171±63	−172±63	21
F_2	0	0	27
CHF_2	−238.9±4		40
CH_2F_2	−453±8		45
CH_3CHF_2	−501±6		45
CF_2	−194.1±9.2		40
COF_2	−634.7	−631.57	67
CHF_3	−697.6		45
CF_3	−467.4±15.1		40
CH_2CF_3	−517.1±5.0		40
CH_3CF_3	−748.7±3.2		41
CH_2FCHF_2	−691±10		41
CF_3O	−655.6±6.3		5
CF_3OH	−923.4±13.4		24
CF_3OF	−785		45
CF_3O_2	−614.0±15.4		46
CF_3CO_2H	−1031		57
$CF_3O_2NO_2$	−686		30
CF_4	−933	−927	59
Cl	121.301±0.008		27
HCl	−92.31±0.10		27
HOCl	−78	−75	32,49
ClO	101.63±0.1		1
ClOO	97.457	99.128	3
OClO	95.6±1.3		33,51
sym-ClO_3	232.6±17		25
ClNO	51.7	53.6	21
$ClNO_2$	12.5	17.95	67
ClONO	56		56
$ClONO_2$	22.9±2.2		2
CH_2Cl	121.8±4.2		64
CH_2ClO_2	9.2		46
CH_3Cl	−81.96±0.67	−74.04±0.67	59
CHF_2Cl	−483.7±5.9		22
CH_3CHFCl	−313.4±2.6		41
CH_3CF_2Cl	−536.2±5.2		41
ClCO	−21.8±2.5	−23.4±2.9	52
COFCl	−427	−423	21
CFCl	−20±29		45
CF_2Cl	−279.1±8.3		40
CF_2ClO_2	−406.5±14.6		46
$CF_2ClO_2NO_2$	−480		43
CF_3Cl	−707.9±3.8	−702.8±3.8	22
Cl_2	0	0	27
Cl_2O	77.2±3.4		62
Cl_2O_2	127.6±2.9		51
Cl_2O_3	153		15
CCl_2	239		40
$CHCl_2$	98.3±5.0		64
$CHCl_2O_2$	1.6		46
CH_2Cl_2	−95.4±0.8	−88.5±0.8	59
$CHFCl_2$	−284.9±8.8		22
$COCl_2$	−220.1	−218.4	32
$CFCl_2$	−89.1±10.0		64
$CFCl_2O_2$	−213.7		46
$CFCl_2O_2NO_2$	−287.4		43
CF_2Cl_2	−493.3±2.5	−489.1±2.5	22
CH_2ClCF_2Cl	−543±10		45
CF_3CHCl_2	−740±10		45
$CF_2ClCHFCl$	−724±10		45
CF_2ClCF_2Cl	−925.5±4.3		41
CCl_3	71.1±2.5	69.9±2.5	36
CCl_3O_2	−11.3±4.6		46
$CCl_3O_2NO_2$	−83.7		43
$CHCl_3$	−103.3±1.3		21
C_2HCl_3	−7.78	−4.318	67
CH_3CCl_3	−144.6±0.8		41
$CFCl_3$	−284.9±1.7	−281.1	22
$CF_2ClCFCl_2$	−726.8±2.8		41
CCl_4	−95.8±0.6	−93.6±0.6	59
C_2Cl_4	−12.4	−11.9	21
C_2Cl_5	33.5±5.4	33.9±6.3	54
Br	111.87±0.12		27
HBr	−36.29±0.16		27
HOBr	⩾−56.19±1.76		60
BrO	125.8±2.4	133.3	18
BrNO	82.17	91.46	67
BrONO	103		29
$BrNO_2$	62.7±7.5		44
$BrONO_2$	47		56
CH_2Br	169.0±4.2		64
CH_3Br	−38.1±1.3		11
CF_3Br	−650		45
CF_2ClBr	−438±8		45
BrCl	14.6±1.3	22.1±1.3	21
Br_2(g)	30.91		27
Br_2O	107.1±3.5		63
$CHBr_2$	188.2±9.2		64
CF_2Br_2	−379±8		45
CF_2BrCF_2Br	−789.9		41
$CHBr_3$	23.8±4.5		11
I	106.76		27
HI	26.50		27
HOI	−90		38
IO	126±18	128±18	7,19
INO	121.3±4.2	124.3±4.2	66
INO_2	60.2±4.2	66.5±4.2	66
CH_2I	230.1±6.7		40
CH_3I	14.2±0.9		26
CF_3I	−589.1±3.3		21
I_2(g)	62.42±0.08		27

*Most of the thermochemical data have been taken from evaluations or reviews. In some cases, we have selected more recent experimental data, which appear to be reliable. The error limits are those given by the original author or reviewer.

References

[1] S. Abramowitz and M. W. Chase, Jr., Pure Appl. Chem. **63**, 1449 (1991).

[2] L. C. Anderson and D. W. Fahey, J. Phys. Chem. **94**, 644 (1990).

[3] S. Baer, H. Hippler, R. Rahn, M. Siefke, N. Seitzinger, and J. Troe, J. Chem. Phys. **95**, 6463 (1991).

[4] Based on equating FO–N bond strengths in FONO and FONO$_2$.

[5] L. Batt and R. Walsh, Int. J. Chem. Kinet. **14**, 933 (1982).

[6] R. Becerra, I. W. Carpenter, and R. Walsh, J. Phys. Chem. A **101**, 4185 (1997).

[7] Y. Bedjanian, G. Le Bras, and G. Poulet, J. Phys. Chem. **100**, 15130 (1996).

[8] S. W. Benson, Chem. Rev. **78**, 23 (1978).

[9] S. W. Benson, *Thermochemical Kinetics*, 2nd ed. (Wiley, New York, 1976).

[10] J. Berkowitz, G. B. Ellison, and D. Gutman, J. Phys. Chem. **98**, 2744 (1994).

[11] J. Bickerton, M. E. Minas Da Piedade, and G. Pilcher, J. Chem. Thermodyn. **16**, 661 (1984).

[12] G. Black, R. Patrick, L. E. Jusinski, and T. G. Slanger, J. Chem. Phys. **80**, 4065 (1984).

[13] R. J. Boyd, A. Gupta, R. F. Langler, S. P. Lownie, and J. A. Pincock, Can. J. Chem. **58**, 331 (1980).

[14] I. F. Bridier, Caralp, H. Loirat, R. Lesclaux, B. Veyret, K. H. Becker, A. Reimer, and F. Zabel, J. Phys. Chem. **95**, 3594 (1991).

[15] J. B. Burkholder, R. L. Mauldin, R. J. Yokelson, S. Solomon, and A. R. Ravishankara, J. Phys. Chem. **97**, 7597 (1993).

[16] Calculated assuming $D(\mathrm{H}\text{-}n\mathrm{C_4H_9}) \approx D(\mathrm{H}\text{-}n\mathrm{C_3H_7}) \approx 420$ kJ mol^{-1}.

[17] Calculated from $\Delta H_f((\mathrm{CH_3})_2\mathrm{SO})$ and the value $D(\mathrm{CH_3{-}SOCH_3}) = 230$ kJ mol^{-1} estimated by Benson (Ref. 8).

[18] M. L. Chase, J. Phys. Chem. Ref. Data **25**, 1069 (1996).

[19] M. L. Chase, J. Phys. Chem. Ref. Data **25**, 1297 (1996).

[20] M. L. Chase, J. Phys. Chem. Ref. Data. **25**, 551 (1996).

[21] M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, J. Phys. Chem. Ref. Data **14**, Suppl. 1 (1985).

[22] S. S. Chen, R. C. Wilhoit, and B. J. Zwolinski, J. Phys. Chem. Ref. Data **5**, 571 (1976).

[23] M.-C. Chuang, M. F. Foltz, and C. B. Moore, J. Chem. Phys. **87**, 3855 (1987).

[24] L. J. Chyall and R. R. Squires, J. Phys. Chem. **100**, 16435 (1996).

[25] A. J. Colussi, J. Phys. Chem. **94**, 8922 (1990).

[26] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic, London, 1970).

[27] *CODATA Key Values for Thermodynamics*, edited by J. D. Cox, D. D. Wagman, and V. A. Medvedev (Hemisphere, New York, 1989).

[28] H. F. Davis, B. Kim, H. S. Johnston, and Y. T. Lee, J. Phys. Chem. **97**, 2172 (1993).

[29] Derived by NASA Panel (see references in Introduction) from an estimated value of $D(\mathrm{BrONO{-}O}) = 305$ kJ mol^{-1}, by analogy with NO$_2$, HONO$_2$, and CH$_3$ONO$_2$.

[30] M. J. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).

[31] R. N. Dixon, J. Chem. Phys. **104**, 6905 (1996).

[32] E. S. Domalski, D. Garvin, and D. D. Wagman, Appendix 1 in R. F. Hampson. and D. Garvin. Natl. Bur. Stand. (U.S.) Spec. Publ. 513 (1978).

[33] R. Flesch, E. Rühl, K. Hottmann, and H. Baumgartel, J. Phys. Chem. **97**, 837 (1993).

[34] D. Fulle, H. F. Hamann, H. Hippler, and C. P. Jänsch, Ber. Bunsenges. Phys. Chem. **101**, 1433 (1997); corrected value.

[35] D. Fulle, H. F. Hamann, H. Hippler, and J. Troe, J. Chem. Phys. **105**, 983 (1997).

[36] J. W. Hudgens, R. D. Johnson, R. S. Timonen, J. A. Seetula, and D. Gutman, J. Phys. Chem. **95**, 4400 (1991).

[37] A. Jefferson, J. M. Nicovich, and P. H. Wine, J. Phys. Chem. **98**, 7128 (1994).

[38] M. E. Jenkin, K. C. Clemitshaw, and R. A. Cox, J. Chem. Soc. Faraday Trans. 2 **80**, 1633 (1984); the above value is the median of the range, -77 to -102 kJ mol^{-1}, deduced in this study.

[39] R. D. Johnson and J. W. Hudgens, J. Phys. Chem. **100**, 19874 (1996).

[40] J. A. Kerr, "Strengths of Chemical Bonds," in *CRC Handbook of Chemistry and Physics*, 77th ed., edited by D. R. Lide (Chemical Rubber Corp., Boca Raton, FL, 1996).

[41] V. P. Kolesov and T. S. Papina, Russ. Chem. Rev. **52**, 425 (1983).

[42] V. P. Kolesov, Russ. Chem. Rev. **47**, 599 (1978).

[43] D. Köppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).

[44] K. D. Kreutter, J. M. Nicovich, and P. H. Wine, J. Phys. Chem. **95**, 4020 (1991); erratum, **96**, 7146 (1992).

[45] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, J. Phys. Chem. Ref. Data **17**, Suppl. 1 (1988).

[46] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).

[47] E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).

[48] J. J. Margitan, J. Phys. Chem. **88**, 3314 (1984).

[49] L. T. Molina and M. J. Molina, J. Phys. Chem. **82**, 2410 (1978).

[50] T. P. Murrells, E. R. Lovejoy, and A. R. Ravishankara, J. Phys. Chem. **94**, 2381 (1990).

[51] S. L. Nickolaisen, R. R. Friedl, and S. P. Sander, J. Phys. Chem. **98**, 155 (1994).

[52] J. M. Nicovich, K. D. Kreutter, and P. H. Wine, J. Chem. Phys. **92**, 3539 (1990).

[53] J. M. Nicovich, K. D. Kreutter, C. A. van Dijk, and P. H. Wine, J. Phys. Chem. **96**, 2518 (1992).

[54] J. M. Nicovich, S. Wang, M. L. McKee, and P. H. Wine, J. Phys. Chem. **100**, 680 (1996).

[55] R. L. Nuttall, A. H. Laufer, and M. V. Kilday, J. Chem. Thermodyn. **3**, 167 (1971).

[56] R. Patrick and D. M. Golden, Int. J. Chem. Kinet. **15**, 1189 (1983).

[57] J. B. Pedley, R. D. Naylor, and S. P. Kirby, *Thermochemical Data of Organic Compounds*, 2nd ed. (Chapman and Hall, London, 1986).

[58] L. G. Piper, J. Chem. Phys. **70**, 3417 (1979).

[59] A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski, J. Phys. Chem. Ref. Data. **3**, 117 (1974).

[60] B. Ruscic and J. Berkowitz, J. Chem. Phys. **101**, 7795 (1994).

[61] N. P. L. Sussex, *Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*, edited by J. B. Pedley and J. Rylance (University of Sussex, England, 1977).

[62] R. P. Thorn, L. J. Stief, S.-C. Kuo, and R. B. Klemm, J. Phys. Chem. **100**, 14178 (1996).

[63] R. P. Thorn, P. S. Monks, L. J. Stief, S.-C. Kuo, Z. Zhang, and R. B. Klemm, J. Phys. Chem. **100**, 12199 (1996).

[64] E. Tschuikow-Roux and S. Paddison, Int. J. Chem. Kinet. **19**, 15 (1987).

[65] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **96**, 7502 (1992).

[66] H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976); H. Hippler, K. Luther, H. Teitelbaum, and J. Troe, Int. J. Chem. Kinet. **9**, 917 (1977).

[67] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, J. Phys. Chem. Ref. Data **11**, Suppl. 2 (1982).

[68] K. W. Watkins and W. W. Thompson, Int. J. Chem. Kinet. **5**, 791 (1973).

[69] Y. Zhao and J. S. Francisco, Chem. Phys. Lett. **173**, 551 (1990).