Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement III

IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry

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This paper updates and extends previous critical evaluations of the kinetics and photochemistry of gas phase chemical reactions of neutral species involved in atmosphere chemistry [J. Phys. Chem. Ref. Data **9**, 295 (1980); **11**, 327 (1982); **13**, 1259 (1984)]. 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 360 thermal and photochemical reactions, containing summaries of the available experimental data with notes giving details of the experimental procedures. For each reaction, a preferred value of the rate coefficient at 298 K is given together with a temperature dependence where possible. The selection of the preferred value is discussed; and estimates of the accuracies of the rate coefficients and temperature coefficients have been made for each reaction. The data sheets are intended to provide the basic physical chemical data needed as input for calculations which model atmospheric chemistry. A table summarizing the preferred rate data is provided, together with an appendix listing the available data on enthalpies of formation of the reactant and product species.

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

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1. Preface

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

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

With the publication of the present evaluation, this data base has been updated and extended to include reactions involved in tropospheric chemistry. It is not possible to cope with all of the very large number of chemical reactions involved in tropospheric chemistry at this stage. Here we have made a start by selecting those organic reactions for which kinetic or photochemical data exist for species containing up to three carbon atoms. Future evaluations will add to this list.

The approach to updating the data sheets in the present supplement has been to revise the data sheets for reactions for which results have been published since September 1983 (the cutoff point for Supplement II[3]) and which alter our previous recommendations. A new type of data sheet has been introduced under the heading "Comment." This summarizes new relevant or related work for a given reaction, but which does not alter our previous recommendation and consequently does not warrant a completely revised data sheet.

It should be emphasized that in preparing the updated data sheets we have not listed all the previous data contained in the original evaluation[1] and the supplements.[2,3] Consequently to obtain the overall picture and background to the preferred rate parameters, it is essential that the previous publications.[1,2,3]

The cutoff point for literature searching for this supplement was March 1988. As in our previous evaluations, however, we also include data which, at the time of our final Subcommittee Meeting (April 1988), was available to us in preprint form.

2. Summary of Reactions and Preferred Rate Data

Summary of Reactions and Preferred Rate Data

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		Δlog k_{298}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
	<u>O_x Reactions</u>						
921	$O + O_2 + M \rightarrow O_3 + M$	6.2×10^{-34} [O_2]	(k_o)	±0.1	$6.2 \times 10^{-34}(T/300)^{-2.0}[O_2]$	200-300	Δn = ±0.5
		5.7×10^{-34} [N_2]	(k_o)	±0.1	$5.7 \times 10^{-34}(T/300)^{-2.8}[N_2]$	200-300	Δn = ±0.5
		2.8×10^{-12}	(k_∞)	±0.2	2.8×10^{-12}	200-300	Δn = ±0.5
		F_c = 0.65		ΔF_c = ±0.1	F_c = exp(-T/696)	200-300	
921	$O + O_2 \rightarrow O_3^*$	See data sheets					
921	$O_3^* + M \rightarrow O_3 + M$	See data sheets					
***	$O + O_3 \rightarrow 2\ O_2$	8.0×10^{-15}		±0.08	8.0×10^{-12}exp(-2060/T)	220-400	±200
**	$O + O_3^* \rightarrow$ products	1.5×10^{-11}		±0.5			
**	$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	4.0×10^{-11}		±0.1	3.2×10^{-11}exp(+67/T)	200-350	±100
***	$O(^1D) + O_3 \rightarrow O_2 + 2\ O(^3P)$	1.2×10^{-10}		±0.1	1.2×10^{-10}	100-400	±100
	$\rightarrow 2\ O_2(^3\Sigma_g^-)$	1.2×10^{-10}		±0.1	1.2×10^{-10}	100-400	±100
922	$O_2^* + O_3 \rightarrow O + 2\ O_2$	See data sheets					
922	$O_2(^1\Delta_g) + M \rightarrow O_2(^3\Sigma_g^-) + M$	1.6×10^{-18}	($M = O_2$)	±0.2	3.0×10^{-18}exp(-200/T)	100-450	±200
		$\leq 1.4 \times 10^{-19}$	($M = N_2$)				
		5×10^{-13}	($M = H_2O$)	±0.3			
		$\leq 2 \times 10^{-20}$	($M = CO_2$)				

Summary of Reactions and Preferred Rate Data -- Continued (2)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
923	$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^3\Sigma_g^-) + M$	8.0×10^{-14}	(M = O)	±0.3			
		4.0×10^{-17}	(M = O_2)	±0.3			
		2.0×10^{-15}	(M = N_2)	±0.1	2.0×10^{-15}	200-350	±200
		4.0×10^{-12}	(M = H_2O)	±0.3			
		4.1×10^{-13}	(M = CO_2)	±0.1	4.1×10^{-13}	245-360	±200
924	$O_2(^1\Sigma_g^+) + O_3 \rightarrow$ products	2.2×10^{-11}		±0.06	2.2×10^{-11}	295-360	±300
**	$O_2(^1\Sigma_g^+)^* + O_2 \rightarrow O_2(^3\Sigma_g^-) + O_2$	See data sheets					
924	$O_2 + h\nu \rightarrow$ products	See data sheets					
926	$O_3 + h\nu \rightarrow$ products	See data sheets					
	<u>HO_x Reactions</u>						
929	$H + HO_2 \rightarrow H_2 + O_2$	5.6×10^{-12}		±0.5	5.6×10^{-12}	245-300	±200
	$\rightarrow 2\ HO$	7.2×10^{-11}		±0.1	7.2×10^{-11}	245-300	±200
	$\rightarrow H_2O + O$	2.4×10^{-12}		±0.5	2.4×10^{-12}	245-300	±200
930	$H + O_2 + M \rightarrow HO_2 + M$	$5.9 \times 10^{-32}[O_2]$	(k_o)	±0.1	$5.9 \times 10^{-32}(T/300)^{-1.0}[O_2]$	200-300	Δn = ±0.6
		$5.9 \times 10^{-32}[N_2]$	(k_o)	±0.1	$5.9 \times 10^{-32}(T/300)^{-1.0}[N_2]$	200-300	Δn = ±0.6

Summary of Reactions and Preferred Rate Data -- Continued (3)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
		7.5×10^{-11} (k_∞)	±0.2	$7.5 \times 10^{-11}(T/300)^{+0.6}$	200-300	$\Delta n = \pm 0.6$
		$F_c = 0.55$	$\Delta F_c = \pm 0.15$	$F_c = \exp(-T/502)$	200-300	
**	$H + O_3 \rightarrow HO + O_2$	2.8×10^{-11}	±0.2	$1.4 \times 10^{-10}\exp(-480/T)$	220-360	±100
930	$H + O_3 \rightarrow HO^* + O_2$	See data sheets				
931	$O + H_2 \rightarrow HO + H$	9×10^{-18}	±0.2			
***	$O + HO \rightarrow O_2 + H$	3.3×10^{-11}	±0.1	$2.3 \times 10^{-11}\exp(+110/T)$	220-500	±100
931	$O + HO_2 \rightarrow HO + O_2$	5.7×10^{-11}	±0.08	$2.9 \times 10^{-11}\exp(+200/T)$	200-400	±100
***	$O + H_2O_2 \rightarrow HO + HC_2$	1.7×10^{-15}	±0.3	$1.4 \times 10^{-12}\exp(-2000/T)$	250-390	±1000
***	$O(^1D) + H_2 \rightarrow HO + H$	1.1×10^{-10}	±0.1	1.1×10^{-10}	200-350	±100
932	$O(^1D) + H_2O \rightarrow 2\ HC$	2.3×10^{-10}	±0.1	2.3×10^{-10}	200-350	±100
***	$HO + H_2 \rightarrow H_2O + H$	6.7×10^{-15}	±0.1	$7.7 \times 10^{-12}\exp(-2100/T)$	200-450	±200
***	$HO + H_2(v=1) \rightarrow H_2C + H$	8.7×10^{-13}	±0.3			
**	$HO + HO \rightarrow H_2O + O$	1.8×10^{-12}	±0.15			
932	$HO + HO + M \rightarrow H_2O_2 + M$	$6.9 \times 10^{-31}[O_2]$ (k_o)	±0.5	$6.9 \times 10^{-31}(T/300)^{-0.8}[O_2]$	200-300	$\Delta n = {}^{+2}_{-0.8}$
		$6.9 \times 10^{-31}[N_2]$ (k_o)	±0.5	$6.9 \times 10^{-31}(T/300)^{-0.8}[N_2]$	200-300	$\Delta n = {}^{+2}_{-0.8}$

Summary of Reactions and Preferred Rate Data -- Continued (4)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
		3.0×10^{-11} (k_∞)	±0.5	3.0×10^{-11}	200-300	$\Delta n = \pm0.5$
		$F_c = 0.72$	$\Delta F_c = \pm0.1$	$F_c = \exp(-T/913)$	200-300	
932	$HO + HO_2 \rightarrow H_2O + O_2$	1.1×10^{-10}	±0.1	$4.8 \times 10^{-11}\exp(+250/T)$	250-400	±200
933	$HO + H_2O_2 \rightarrow H_2O + HO_2$	1.7×10^{-12}	±0.1	$2.9 \times 10^{-12}\exp(-160/T)$	240-460	±100
933	$HO + O_3 \rightarrow HO_2 + O_2$	6.7×10^{-14}	±0.15	$1.9 \times 10^{-12}\exp(-1000/T)$	220-450	±300
**	$HO^* + M \rightarrow HO + M$	See data sheets				
934	$HO^* + O_3 \rightarrow$ products	See data sheets				
934	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.6×10^{-12}	±0.15	$2.2 \times 10^{-13}\exp(+600/T)$	230-420	±200
934	$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$	$4.5 \times 10^{-32}[O_2]$	±0.15			
		$5.2 \times 10^{-32}[N_2]$	±0.15	$1.9 \times 10^{-33}\exp(+980/T)[N_2]$	230-420	±300
		See data sheets for effect of H_2O				
936	$HO_2 + O_3 \rightarrow HO + 2\,O_2$	2.0×10^{-15}	±0.2	$1.4 \times 10^{-14}\exp(-600/T)$	250-350	$^{+500}_{-100}$
**	$H_2O + h\nu \rightarrow HO + H$	See data sheets				
936	$H_2O_2 + h\nu \rightarrow 2\,HO$	See data sheets				

Summary of Reactions and Preferred Rate Data -- Continued (5)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/ K
	NO_x Reactions						
***	$O + NO + M \rightarrow NO_2 + M$	$8.6 \times 10^{-32}[O_2]$	(k_o)	±0.2	$8.6 \times 10^{-32}(T/300)^{-1.8}[O_2]$	200-300	$\Delta n = \pm 0.5$
		$1.0 \times 10^{-31}[N_2]$	(k_o)	±0.1	$1.0 \times 10^{-31}(T/300)^{-1.6}[N_2]$	200-300	$\Delta n = \pm 0.5$
		3.0×10^{-11}	(k_∞)	±0.2	$3.0 \times 10^{-11}(T/300)^{+0.3}$	300-1500	$\Delta n = \pm 0.5$
		$F_c = 0.85$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/1850)$	200-300	
937	$O + NO_2 \rightarrow O_2 + NO$	9.7×10^{-12}		±0.06	$6.5 \times 10^{-12}\exp(+120/T)$	230-350	±120
*	$O + NO_2 + M \rightarrow NO_3 + M$	$9 \times 10^{-32}[O_2]$	(k_o)	±0.3	$9 \times 10^{-32}(T/300)^{-2.0}[O_2]$	200-400	$\Delta n = \pm 1.0$
		$9 \times 10^{-32}[N_2]$	(k_o)	±0.1	$9 \times 10^{-32}(T/300)^{-2.0}[N_2]$	200-400	$\Delta n = \pm 1.0$
		2.2×10^{-11}	(k_∞)	±0.1	2.2×10^{-11}	200-400	$\Delta n = \pm 0.5$
		$F_c = 0.8$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/1300)$	200-400	
*	$O + NO_3 \rightarrow O_2 + NO_2$	1×10^{-11}		±0.5			
*	$O + N_2O_5 \rightarrow$ products	$\leq 3 \times 10^{-16}$			$\leq 3 \times 10^{-16}$	220-300	
**	$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	2.6×10^{-11}		±0.1	$1.8 \times 10^{-11}\exp(+107/T)$	200-350	±100
**	$O(^1D) + N_2O \rightarrow N_2 + O_2$	4.4×10^{-11}		±0.15	4.4×10^{-11}	200-350	±100
	$\rightarrow 2\ NO$	7.2×10^{-11}		±0.15	7.2×10^{-11}	200-350	±100
**	$N + HO \rightarrow NO + H$	4.9×10^{-11}		±0.15	$3.8 \times 10^{-11}\exp(+85/T)$	250-500	±100

Summary of Reactions and Preferred Rate Data -- Continued (6)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
938	$N + O_2 \rightarrow NO + O$	8.9×10^{-17}		±0.1	$4.4 \times 10^{-12}\exp(-3220/T)$	280-333	±350
**	$N + O_2(^1\Delta_g) \rightarrow NO + O$	$\leq 1 \times 10^{-16}$			$\leq 1 \times 10^{-16}$	200-300	
938	$N + O_3 \rightarrow NO + O_2$	1×10^{-16}		±0.3			
**	$N + NO \rightarrow N_2 + O$	3.1×10^{-11}		±0.15	3.1×10^{-11}	200-400	±100
***	$N + NO_2 \rightarrow N_2O + O$	3.0×10^{-12}		±0.2			
939	$HO + NH_3 \rightarrow H_2O + NH_2$	1.6×10^{-13}		±0.15	$3.5 \times 10^{-12}\exp(-925/T)$	230-450	±200
939	$HO + HONO \rightarrow H_2O + NO_2$	4.9×10^{-12}		±0.3	$1.8 \times 10^{-11}\exp(-390/T)$	280-340	±400
940	$HO + HONO_2 \rightarrow H_2O + NO_3$	1.5×10^{-13}	(1 atm)	±0.1	See data sheets		
941	$HO + HO_2NO_2 \rightarrow$ products	5.0×10^{-12}		±0.2	$1.5 \times 10^{-12}\exp(+360/T)$	240-340	+300 -600
***	$HO + NO + M \rightarrow HONO + M$	$7.4 \times 10^{-31}[O_2]$	(k_o)	±0.2	$7.4 \times 10^{-31}(T/300)^{-2.4}[O_2]$	200-440	Δn = ±1.0
		$7.4 \times 10^{-31}[N_2]$	(k_o)	±0.1	$7.4 \times 10^{-31}(T/300)^{-2.4}[N_2]$	200-440	Δn = ±0.5
		1.0×10^{-11}	(k_∞)	±0.2	1.0×10^{-11}	200-400	Δn = ±0.5
		$F_c = 0.8$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/1300)$	200-400	
942	$HO + NO_2 + M \rightarrow HONO_2 + M$	$2.2 \times 10^{-30}[O_2]$	(k_o)	±0.1	$2.2 \times 10^{-30}(T/300)^{-2.9}[O_2]$	200-300	Δn = ±0.5
		$2.6 \times 10^{-30}[N_2]$	(k_o)	±0.1	$2.6 \times 10^{-30}(T/300)^{-2.9}[N_2]$	200-300	Δn = ±0.5

Summary of Reactions and Preferred Rate Data -- Continued (7)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta \log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
		5.2×10^{-11}	(k_∞)	±0.2	5.2×10^{-11}	200-300	$\Delta n = \pm 0.5$
		$F_c = 0.43$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/353)$	200-300	
942	$HO + NO_3 \rightarrow HO_2 + NO_2$	2.3×10^{-11}		±0.2			
**	$HO_2 + NO \rightarrow HO + NO_2$	8.3×10^{-12}		±0.1	$3.7 \times 10^{-12}\exp(+240/T)$	230-500	±100
943	$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$	$1.5 \times 10^{-31}[O_2]$	(k_0)	±0.1	$1.5 \times 10^{-31}(T/300)^{-3.2}[O_2]$	220-360	$\Delta n = \pm 1$
		$1.8 \times 10^{-31}[N_2]$	(k_0)	±0.1	$1.8 \times 10^{-31}(T/300)^{-3.2}[N_2]$	220-360	$\Delta n = \pm 1$
		4.7×10^{-12}	(k_∞)	±0.1	4.7×10^{-12}	200-300	$\Delta n = \pm 1$
		$F_c = 0.6$		$\Delta F_c = \pm 0.1$	See data sheets		
**	$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$	$9.3 \times 10^{-21}[O_2]$	(k_0/s^{-1})	±0.3	$3.6 \times 10^{-6}\exp(-10000/T)[O_2]s^{-1}$	260-300	±500
		$1.3 \times 10^{-20}[N_2]$	(k_0/s^{-1})	±0.3	$5 \times 10^{-6}\exp(-10000/T)[N_2]s^{-1}$	260-300	±500
		0.23	(k_∞/s^{-1})	±0.6	$3.4 \times 10^{14}\exp(-10420/T)s^{-1}$	250-300	±500
		$F_c = 0.6$		$\Delta F_c = \pm 0.1$			
944	$\left.\begin{array}{r} HO_2 + NO_3 \rightarrow O_2 + HONO_2 \\ HO + NO_2 + O_2 \end{array}\right\}$	4.3×10^{-12}		±0.2			
**	$NH_2 + HO \rightarrow$ products	No recommendation (see data sheets)					
**	$NH_2 + HO_2 \rightarrow$ products	3.4×10^{-11}		±0.4			

Summary of Reactions and Preferred Rate Data -- Continued (8)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
944	$NH_2 + O_2 \rightarrow$ products	$<3 \times 10^{-18}$				
945	$NH_2 + O_3 \rightarrow$ products	1.7×10^{-13}	±0.5	$4.9 \times 10^{-12}\exp(-1000/T)$	250-380	±500
946	$NH_2 + NO \rightarrow$ products	1.6×10^{-11}	±0.3	$1.6 \times 10^{-11}(T/298)^{-1.5}$	210-500	$\Delta n = \pm 0.5$
947	$NH_2 + NO_2 \rightarrow$ products	1.9×10^{-11}	±0.3	$1.9 \times 10^{-11}(T/298)^{-2.2}$	250-500	$\Delta n = \pm 1.5$
948	$2\ NO + O_2 \rightarrow 2\ NO_2$	2.0×10^{-38} (cm^6 molecule^{-2} s^{-1})	±0.1	$3.3 \times 10^{-39}\exp(+530/T)$	273-600	±400
949	$NO + NO_3 \rightarrow 2\ NO_2$	2.7×10^{-11}	±0.12	$1.6 \times 10^{-11}\exp(+150/T)$	200-300	±100
949	$NO_2 + O_3 \rightarrow NO_3 + O_2$	3.2×10^{-17}	±0.06	$1.2 \times 10^{-13}\exp(-2450/T)$	230-360	±150
950	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	$2.7 \times 10^{-30}[N_2]$ (k_o)	±0.1	$2.7 \times 10^{-30}(T/300)^{-3.4}[N_2]$	200-300	$\Delta n = \pm 0.5$
		2.0×10^{-12} (k_∞)	±0.1	$2.0 \times 10^{-12}(T/300)^{+0.2}$	200-500	$\Delta n = \pm 0.6$
		$F_c = 0.34$				
**	$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	$1.6 \times 10^{-19}[N_2]$ (k_o/s^{-1})	±0.2	$2.2 \times 10^{-3}(T/300)^{-4.4}\exp(-11080/T)[N_2]s^{-1}$	200-300	±500
		6.9×10^{-2} (k_∞/s^{-1})	±0.3	$9.7 \times 10^{14}(T/300)^{+0.1}\exp(-11080/T)s^{-1}$	200-300	±500
		$F_c = 0.34$				
952	$N_2O_5 \rightleftarrows NO_2 + NO_3$	See data sheets				
952	$N_2O_5 + H_2O \rightarrow 2\ HONO_2$	$<2 \times 10^{-21}$				

Summary of Reactions and Preferred Rate Data -- Continued (9)

Page number	Reaction	k_{298} cm^3 $molecule^{-1}$ s^{-1}	$\Delta \log k_{298}$	Temp. dependence of k/cm^3 $mclecule^{-1}$ s^{-1}	Temp. range/K	$\Delta(E/R)$/K
953	HONO + hν → products	See data sheets				
953	$HONO_2$ + hν → products	See data sheets				
954	HO_2NO_2 + hν → products	See data sheets				
**	NO + hν → products	See data sheets				
954	NO_2 + hν → products	See data sheets				
956	NO_3 + hν → products	See data sheets				
957	N_2O + hν → products	See data sheets				
957	N_2O_5 + hν → products	See data sheets				
	<u>Organic Reactions</u>					
958	$O + CH_3 \rightarrow HCHO + H$	1.4×10^{-10}	±0.1	1.4×10^{-10}	200-900	±100
***	$O + CN \rightarrow CO + N(^2D)$	1.4×10^{-11}	±0.2			
	$\rightarrow CO + N(^4S)$	3.4×10^{-12}	±0.2			
959	$O(^1D) + CH_4 \rightarrow HO + CH_3$	1.4×10^{-10}	±0.1	1.4×10^{-10}	200-300	±100
	$\rightarrow HCHO + H_2$	1.5×10^{-11}	±0.1	1.5×10^{-11}	200-300	±100
959	$HO + CH_4 \rightarrow H_2O + CH_3$	8.3×10^{-15}	±0.1	$3.7 \times 10^{-12}\exp(-1820/T)$	240-300	±100

Summary of Reactions and Preferred Rate Data -- Continued (10)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
961	$HO + C_2H_2 + M \rightarrow C_2H_2OH + M$	$5 \times 10^{-30}[N_2]$	(k_o)	±0.1	$5 \times 10^{-30}[N_2]$	220-300	$\Delta n = \pm 1$
		8.3×10^{-13}	(k_∞)	±0.1	$8.3 \times 10^{-13}(T/300)^{+2}$	220-300	$\Delta n = \pm 1$
		$F_c = 0.6$		$\Delta F_c = \pm 0.2$			
962	$HO + C_2H_4 + M \rightarrow C_2H_4OH + M$	$9.5 \times 10^{-29}[O_2]$	(k_o)	±0.3	$9.5 \times 10^{-29}(T/300)^{-3.1}[O_2]$	200-300	$\Delta n = \pm 2$
		$9.5 \times 10^{-29}[N_2]$	(k_o)	±0.3	$9.5 \times 10^{-29}(T/300)^{-3.1}[N_2]$	200-300	$\Delta n = \pm 2$
		9×10^{-12}	(k_∞)	±0.3	9×10^{-12}	200-300	$\Delta n = \pm 1$
		$F_c = 0.7$		$\Delta F_c = 0.2$	$F_c = \exp(-T/840)$	200-300	
962	$HO + C_2H_6 \rightarrow H_2O + C_2H_5$	2.7×10^{-13}		±0.1	$7.4 \times 10^{-12}\exp(-990/T)$	230-300	±100
964	$HO + C_3H_6 + M \rightarrow C_3H_6OH + M$	$8 \times 10^{-27}[O_2]$	(k_o)	±1	$8 \times 10^{-27}(T/300)^{-3.5}[O_2]$	200-300	$\Delta n = \pm 1$
		$8 \times 10^{-27}[N_2]$	(k_o)	±1	$8 \times 10^{-27}(T/300)^{-3.5}[N_2]$	200-300	$\Delta n = \pm 1$
		3.0×10^{-11}	(k_∞)	±0.1	3.0×10^{-11}	200-300	$\Delta n = \pm 1$
		$F_c = 0.5$		$\Delta F_c = \pm 0.2$	$F_c = \exp(-T/433)$		
964	$HO + C_3H_8 \rightarrow H_2O + C_3H_7$	1.1×10^{-12}		±0.15	$8.6 \times 10^{-12}\exp(-610/T)$	~300	±200
966	$HO + CO \rightarrow H + CO_2$	$(1.5 \times 10^{-13}) \times$ $[1 + 0.6(P/atm)]$	(0-760 Torr, air)	±0.1	$(1.5 \times 10^{-13}) \times$ $[1 + 0.6\ (P/atm)]$ (0-760 Torr, air)	200-300	±300
967	$HO + HCHO \rightarrow H_2O + HCO$	1.1×10^{-11}		±0.1	$1.6 \times 10^{-11}\exp(-110/T)$	230-580	±150

Summary of Reactions and Preferred Rate Data -- Continued (11)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
968	$HO + CH_3CHO \rightarrow H_2O + CH_3CO$	1.6×10^{-11}	±0.1	$5.6 \times 10^{-12}\exp(+310/T)$	240-530	±200
969	$HO + C_2H_5CHO \rightarrow$ products	2.0×10^{-11}	±0.15			
969	$HO + (CHO)_2 \rightarrow$ products	1.1×10^{-11}	±0.3			
970	$HO + HOCH_2CHO \rightarrow H_2O + HOCH_2CO$	8.0×10^{-12}	±0.3			
	$\rightarrow H_2O + HOCHCHO$	2.0×10^{-12}	±0.3			
970	$HO + CH_3COCHO \rightarrow H_2O + CH_3COCO$	1.7×10^{-11}	±0.3			
971	$HO + CH_3COCH_3 \rightarrow H_2O + CH_2COCH_3$	2.3×10^{-13}	±0.2	$1.7 \times 10^{-12}\exp(-600/T)$	240-440	±300
972	$\left.\begin{array}{l} HO + CH_3OH \rightarrow H_2O + CH_2OH \\ \quad\rightarrow H_2O + CH_3O \end{array}\right\}$	9.0×10^{-13}	±0.2	$9.1 \times 10^{-12}\exp(-690/T)$	240-1000	±250
973	$HO + C_2H_5OH \rightarrow$ products	3.4×10^{-12}	±0.2	$9.3 \times 10^{-12}\exp(-300/T)$	250-450	±200
974	$HO + n\text{-}C_3H_7OH \rightarrow$ products	5.3×10^{-12}	±0.2			
974	$HO + i\text{-}C_3H_7OH \rightarrow$ products	5.6×10^{-12}	±0.2	5.6×10^{-12}	240-440	±200
975	$HO + CH_3OOH \rightarrow H_2O + CH_2OOH$	4.4×10^{-12}	±0.3			
	$\rightarrow H_2O + CH_3OO$	6.6×10^{-12}	±0.3			
976	$HO + HCOOH \rightarrow$ products	4.8×10^{-13}	±0.2	4.8×10^{-13}	290-430	±150
976	$HO + CH_3COOH \rightarrow$ products	7.4×10^{-13}	±0.3	$1.3 \times 10^{-12}\exp(-170/T)$	290-440	±300

Summary of Reactions and Preferred Rate Data -- Continued (12)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
977	$HO + CH_3CO_3NO_2 \rightarrow$ products	1.4×10^{-13}	±0.2	$1.2 \times 10^{-12}\exp(-650/T)$	270-300	±400
977	$HO + HCN \rightarrow$ products	3×10^{-14} (1 atm)	±0.5	$1.2 \times 10^{-13}\exp(-400/T)$(1 atm)	296-433	±300
977	$HO + CH_3CN \rightarrow$ products	2.0×10^{-14}	±0.2	$6.3 \times 10^{-13}\exp(-1030/T)$	250-360	±250
978	$HO_2 + CH_3O_2 \rightarrow O_2 + CH_3O_2H$	4.9×10^{-12}	±0.3	$1.7 \times 10^{-13}\exp(+1000/T)$	250-380	±500
979	$HO_2 + C_2H_5O_2 \rightarrow O_2 + C_2H_5O_2H$	5.8×10^{-12}	±0.2	$6.5 \times 10^{-13}\exp(+650/T)$	240-380	±200
980	$HO_2 + HCHO \rightarrow HOCH_2OO$	7.9×10^{-14}	±0.2	$9.7 \times 10^{-15}\exp(+625/T)$	275-333	±600
981	$HOCH_2OO \rightarrow HO_2 + HCHO$	1.5×10^{2} s^{-1}	±0.2	$2.4 \times 10^{12}\exp(-7000/T)$s^{-1}	275-333	±2000
981	$NO_3 + C_2H_2 \rightarrow$ products	$<1 \times 10^{-16}$				
982	$NO_3 + C_2H_4 \rightarrow$ products	2.1×10^{-16}	±0.3			
983	$NO_3 + C_3H_6 \rightarrow$ products	9.4×10^{-15}	±0.2			
984	$NO_3 + HCHO \rightarrow HNO_3 + HCO$	6×10^{-16}	±0.3			
985	$NO_3 + CH_3CHO \rightarrow HNO_3 + CH_3CO$	2.7×10^{-15}	±0.2	$1.4 \times 10^{-12}\exp(-1860/T)$	260-370	±500
985	$NO_3 + CH_3OH \rightarrow$ products	$<1 \times 10^{-15}$				
986	$NO_3 + C_2H_5OH \rightarrow$ products	$<2 \times 10^{-15}$				
986	$NO_3 + i\text{-}C_3H_7OH \rightarrow$ products	$<5 \times 10^{-15}$				

Summary of Reactions and Preferred Rate Data -- Continued (13)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
987	$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	$8 \times 10^{-31}[N_2]$	(k_o)	±0.2	$8 \times 10^{-31}(T/300)^{-3.3}[N_2]$	200-600	$\Delta n = \pm 1$
		2.2×10^{-12}	(k_∞)	±0.3	$2.2 \times 10^{-12}(T/300)^1$	200-400	$\Delta n = \pm 1$
		$F_c = 0.27$		$\Delta F_c = \pm 0.1$			
988	$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	$<2 \times 10^{-15}$			$1.4 \times 10^{-12}\exp(-1950/T)$	300-2500	±600
989	$C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$	$2.0 \times 10^{-28}[O_2]$	(k_o)	±0.3	$2.0 \times 10^{-28}(T/300)^{-3.8}[O_2]$	200-300	$\Delta n = \pm 1$
		$2.0 \times 10^{-28}[N_2]$	(k_o)	±0.3	$2.0 \times 10^{-28}(T/300)^{-3.8}[N_2]$	200-300	$\Delta n = \pm 1$
		5×10^{-12}	(k_∞)	±0.3	5×10^{-12}	200-300	$\Delta n = \pm 1$
		$F_c = 0.7$		$\Delta F_c = \pm 0.2$	$F_c = \exp(-T/840)$		
989	$n\text{-}C_3H_7 + O_2 + M \rightarrow n\text{-}C_3H_7O_2 + M$	6×10^{-12}	(k_∞)	±0.3	6×10^{-12}	200-300	$\Delta n = \pm 1$
989	$i\text{-}C_3H_7 + O_2 + M \rightarrow i\text{-}C_3H_7O_2 + M$	1.5×10^{-11}	(k_∞)	±0.3	1.5×10^{-11}	200-300	$\Delta n = \pm 1$
***	$HCO + O_2 \rightarrow CO + HO_2$	5.6×10^{-12}		±0.2	$3.5 \times 10^{-12}\exp(+140/T)$	300-500	±150
***	$CH_3CO + O_2\ (+M) \rightarrow CH_3CO_3\ (+M)$	2×10^{-12}	(1-4 Torr)				
		5×10^{-12}	(k_∞)	±0.5	5×10^{-12}	200-300	$\Delta n = \pm 1$
989	$CH_3O + O_2 \rightarrow HCHO + HO_2$	1.9×10^{-15}		±0.2	$7.2 \times 10^{-14}\exp(-1080/T)$	298-610	±300
990	$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	8.0×10^{-15}		±0.3			
991	$n\text{-}C_3H_7O + O_2 \rightarrow C_2H_5CHO + HO_2$	8×10^{-15}		±0.5			

Summary of Reactions and Preferred Rate Data -- Continued (14)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/ K
992	$i\text{-}C_3H_7O + O_2 \rightarrow CH_3COCH_3 + HO_2$	8×10^{-15}		±0.3	$1.5 \times 10^{-14}\exp(-200/T)$	290-390	±200
992	$CH_2OH + O_2 \rightarrow HCHO + HO_2$	9.8×10^{-12}		±0.15			
993	$CH_3 + O_3 \rightarrow$ products	2.5×10^{-12}		±0.3	$5.1 \times 10^{-12}\exp(-210/T)$	240-400	±200
993	$CH_3O + NO + M \rightarrow CH_3ONO + M$	$3 \times 10^{-28}[He]$	(k_o)	±0.5			
		$6 \times 10^{-28}[N_2]$	(k_o)	±0.5			
		2×10^{-11}	(k_∞)	±0.3	2×10^{-11}	200-400	
		$F_c = 0.6$					
994	$RO + NO + M \rightarrow RONO + M$	See data sheets					
994	$RO + NO \rightarrow R'O + HNO$	See data sheets					
995	$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + N$	$2.6 \times 10^{-29}[He]$	(k_o)	±0.5	$2.6 \times 10^{-29}(T/300)^{-4.5}[He]$	200-400	$\Delta n = \pm 2$
		1.5×10^{-11}	(k_∞)	±0.3	1.5×10^{-11}	300-400	
		$F_c = 0.4$					
995	$CH_3O + NO_2 \rightarrow HCHO + HONO$	$<3 \times 10^{-13}$			$<3 \times 10^{-13}$	200-300	
996	$RO + NO_2 + M \rightarrow RONO_2 + M$	See data sheets					
996	$RO + NO_2 \rightarrow R'O + HONO$	See data sheets					
996	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	7.6×10^{-12}		±0.1	$4.2 \times 10^{-12}\exp(+180/T)$	240-360	±180

Summary of Reactions and Preferred Rate Data -- Continued (15)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/ K
996	$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$	8.9×10^{-12}		±0.3			
996	$C_2H_5O_2 + NO\ (+M) \rightarrow C_2H_5ONO_2\ (+M)$	$\leq 1.3 \times 10^{-13}$	(1 atm, air)				
996	$n\text{-}C_3H_7O_2 + NO \rightarrow n\text{-}C_3H_7O + NO_2$	8.7×10^{-12}		±0.3			
996	$n\text{-}C_3H_7O_2 + NO\ (+M) \rightarrow n\text{-}C_3H_7ONO_2\ (+M)$	1.8×10^{-13}	(1 atm, air)	±0.3			
996	$i\text{-}C_3H_7O_2 + NO \rightarrow i\text{-}C_3H_7O + NO_2$	8.5×10^{-12}		±0.3			
996	$i\text{-}C_3H_7O_2 + NO\ (+M) \rightarrow i\text{-}C_3H_7ONO_2\ (+M)$	3.8×10^{-13}	(1 atm, air)	±0.3			
**	$CH_3CO_3 + NO \rightarrow CH_3 + CO_2 + NO_2$	1.4×10^{-11}		±0.7			
**	$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$	$2.3 \times 10^{-30}[O_2]$	(k_o)	±0.2	$2.3 \times 10^{-30}(T/300)^{-4.0}[O_2]$	200-300	$\Delta n = \pm 2$
		$2.3 \times 10^{-30}[N_2]$	(k_o)	±0.1	$2.3 \times 10^{-30}(T/300)^{-4.0}[N_2]$	200-300	$\Delta n = \pm 2$
		8×10^{-12}	(k_∞)	±0.2	8×10^{-12}	200-300	$\Delta n = \pm 0.5$
		$F_c = 0.4$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/327)$		
997	$CH_3O_2NO_2 + M \rightarrow CH_3O_2 + NO_2 + M$	$6.8 \times 10^{-19}[N_2]$	(k_o/s^{-1})	±0.3	$9 \times 10^{-5}\exp(-9690/T)[N_2]s^{-1}$	250-300	±500
		4.5	(k_∞/s^{-1})	±0.3	$1.1 \times 10^{16}\exp(-10560/T)s^{-1}$	250-300	±500
		$F_c = 0.4$					

Summary of Reactions and Preferred Rate Data -- Continued (16)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
***	$C_2H_5O_2 + NO_2 + M \rightarrow C_2H_5O_2NO_2 + M$	5×10^{-12}	(k_∞)	±0.5	5×10^{-12}	200-300	$\Delta n = \pm 1$
998	$C_2H_5O_2NO_2 + M \rightarrow C_2H_5O_2 + NO_2 + M$	No recommendation (see data sheets)					
998	$CH_3CO_3 + NO_2 + M \rightarrow CH_3CO_3NO_2 + M$	$2 \times 10^{-28}[N_2]$	(k_0)	±0.5			
		8.4×10^{-12}	(k_∞)	±0.3			
		$F_c = 0.27$					
999	$CH_3CO_3NO_2 + M \rightarrow CH_3CO_3 + NO_2 + M$	$1.5 \times 10^{-20}[N_2]$	(k_0/s^{-1})	±0.5	$6.3 \times 10^{-2}\exp(-12785/T)[N_2]s^{-1}$	300-320	±1000
		5.8×10^{-4}	(k_∞/s^{-1})	±0.3	$2.2 \times 10^{16}\exp(-13435/T)s^{-1}$	300-320	±500
		$F_c = 0.27$					
1000	$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2$	$\geq 2.1 \times 10^{-13}$		±0.3	$1.7 \times 10^{-13}\exp(+220/T)$	200-400	±220
	$\rightarrow 2\ CH_3O + O_2$	1.3×10^{-13}		±0.3			
	$\rightarrow CH_3OOCH_3 + O_2$	$\leq 3 \times 10^{-14}$					
1001	$CH_3O_2 + CH_3CO_3 \rightarrow CH_3O + CH_3CO_2 + O_2$	5.5×10^{-12}		±0.5			
	$\rightarrow CH_3CO_2H + HCHO + O_2$	5.5×10^{-12}		±0.5			

Summary of Reactions and Preferred Rate Data -- Continued (17)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/ K
1002	$C_2H_5O_2 + C_2H_5O_2 \rightarrow C_2H_5OH + CH_3CHO + O_2$	8.6 x 10^{-14}	±0.12	1.2 x 10^{-13}exp(-110/T)	250-450	+300 -100
	$\rightarrow 2\ C_2H_5O + O_2$					
	$\rightarrow C_2H_5OOC_2H_5 + O_2$					
1003	$n\text{-}C_3H_7O_2 + n\text{-}C_3H_7O_2 \rightarrow n\text{-}C_3H_7OH + C_2H_5CHO + O_2$	3 x 10^{-13}	±0.5			
	$\rightarrow 2\ n\text{-}C_3H_7O + O_2$					
1004	$i\text{-}C_3H_7O_2 + i\text{-}C_3H_7O_2 \rightarrow i\text{-}C_3H_7OH + CH_3COCH_3 + O_2$	4.4 x 10^{-16}	±0.3	6.0 x 10^{-14}exp(-1460/T)	300-400	±300
	$\rightarrow 2\ i\text{-}C_3H_7O + O_2$	5.6 x 10^{-16}	±0.3	3.2 x 10^{-12}exp(-2580/T)	300-400	±300
1005	$CH_3CO_3 + CH_3CO_3 \rightarrow 2\ CH_3CO_2 + O_2$	1.6 x 10^{-11}	±0.5	2.8 x 10^{-12}exp(+530/T)	250-370	±500
1006	$RCHOO + H_2O \rightarrow RCOOH + H_2O$	No recommendation (see data sheets)				
1006	$RCHOO + NO_2 \rightarrow RCHO + NO_3$					
1006	$RCHOO + SO_2 \rightarrow$ products					
1006	$RCHOO + HCHO \rightarrow$ products					

Summary of Reactions and Preferred Rate Data -- Continued (18)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	Δlog k_{298}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	Δ(E/R)/K
1008	$CN + O_2 \rightarrow$ products	2.1×10^{-11}	±0.15	$1.1 \times 10^{-11}\exp(+205/T)$	290-760	±200
1009	$O_3 + C_2H_2 \rightarrow$ products	1×10^{-20}	±1.0			
1009	$O_3 + C_2H_4 \rightarrow$ products	1.7×10^{-18}	±0.1	$1.2 \times 10^{-14}\exp(-2630/T)$	180-360	±100
1011	$O_3 + C_3H_6 \rightarrow$ products	1.1×10^{-17}	±0.15	$1.3 \times 10^{-14}\exp(-2105/T)$	250-360	±400
1012	$HCHO + h\nu \rightarrow$ products	See data sheets				
1015	$CH_3CHO + h\nu \rightarrow$ products	See data sheets				
1016	$C_2H_5CHO + h\nu \rightarrow$ products	See data sheets				
1017	$(CHO)_2 + h\nu \rightarrow$ products	See data sheets				
1019	$CH_3COCHO + h\nu \rightarrow$ products	See data sheets				
1020	$CH_3COCH_3 + h\nu \rightarrow$ products	See data sheets				
**	$CH_3OOH + h\nu \rightarrow$ products	See data sheets				
**	$CH_3O_2NO_2 + h\nu \rightarrow$ products	See data sheets				
1021	$CH_3CO_3NO_2 + h\nu \rightarrow$ products	See data sheets				
	SO_x Reactions					
**	$O + H_2S \rightarrow HO + HS$	2.2×10^{-14}	±0.3	$1.4 \times 10^{-11}\exp(-1920/T)$	290-500	±750
*	$O + CS \rightarrow CO + S$	2.1×10^{-11}	±0.1	$2.7 \times 10^{-10}\exp(-760/T)$	150-300	±250

Summary of Reactions and Preferred Rate Data -- Continued (19)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
***	$O + CH_3SCH_3 \rightarrow CH_3SO + CH_3$	5.0×10^{-11}		±0.1	$1.3 \times 10^{-11}\exp(+409/T)$	270-560	±100
***	$O + CS_2 \rightarrow SO + CS$	3.6×10^{-12}		±0.2	$3.2 \times 10^{-11}\exp(-650/T)$	200-500	±100
***	$O + CH_3SSCH_3 \rightarrow CH_3SO + CH_3S$	1.3×10^{-10}		±0.3	$5.5 \times 10^{-11}\exp(+250/T)$	290-570	±100
*	$O + OCS \rightarrow SO + CO$	1.4×10^{-14}		±0.2	$2.6 \times 10^{-11}\exp(-2250/T)$	220-600	±150
*	$O + SO_2 + M \rightarrow SO_3 + M$	$1.4 \times 10^{-33}[O_2]$	(k_o)	±0.3	$4.0 \times 10^{-32}\exp(-1000/T)[O_2]$	200-400	$^{+200}_{-100}$
		$1.4 \times 10^{-33}[N_2]$	(k_o)	±0.3	$4.0 \times 10^{-32}\exp(-1000/T)[N_2]$	200-400	$^{+200}_{-100}$
**	$S + O_2 \rightarrow SO + O$	2.3×10^{-12}		±0.2	2.3×10^{-12}	230-400	±200
*	$S + O_3 \rightarrow SO + O_2$	1.2×10^{-11}		±0.3			
1022	$HO + H_2S \rightarrow H_2O + HS$	4.8×10^{-12}		±0.08	$6.3 \times 10^{-12}\exp(-80/T)$	200-300	±80
1023	$HO + CH_3SH \rightarrow$ products	3.3×10^{-11}		±0.1	$9.9 \times 10^{-12}\exp(+356/T)$	240-430	±100
1024	$HO + CH_3SCH_3 \rightarrow H_2O + CH_2SCH_3$	4.4×10^{-12}		±0.1	$9.6 \times 10^{-12}\exp(-234/T)$	250-400	±300
	$\rightarrow CH_3S(OH)CH_3$	1.7×10^{-12}	(1 atm, air)	±0.3	See data sheets		
1025	$HO + CS_2 \rightarrow$ products	$\leq 7.0 \times 10^{-15}$	$([O_2] = 0)$				
		2.0×10^{-12}	(1 atm, air)	±0.3	$8.8 \times 10^{-16}\exp(+2300/T)$	260-300	±500
***	$HO + CH_3SSCH_3 \rightarrow$ products	2.0×10^{-10}		±0.1	$6.0 \times 10^{-11}\exp(+380/T)$	250-370	±300
1026	$HO + OCS \rightarrow$ products	2.0×10^{-15}		±0.3	$1.1 \times 10^{-13}\exp(-1200/T)$	250-500	±500

Summary of Reactions and Preferred Rate Data -- Continued (20)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1026	$HO + SO_2 + M \rightarrow HOSO_2 + M$	$5.0 \times 10^{-31}[O_2]$ (k_0)	±0.3	$5.0 \times 10^{-31}(T/300)^{-3.3}[O_2]$	200-300	$\Delta n = \pm 0.5$
		$5.0 \times 10^{-31}[N_2]$ (k_0)	±0.3	$5.0 \times 10^{-31}(T/300)^{-3.3}[N_2]$	200-300	$\Delta n = \pm 0.5$
		2×10^{-12} (k_∞)	±0.3	2×10^{-12}	200-300	$\Delta n = \pm 1$
		$F_c = 0.45$	$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/380)$	200-300	
1027	$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$	4.0×10^{-13}	±0.1			
**	$HO_2 + SO_2 \rightarrow$ products	$\leq 1 \times 10^{-18}$				
1027	$NO_3 + H_2S \rightarrow$ products	$< 1 \times 10^{-15}$				
1028	$NO_3 + CS_2 \rightarrow$ products	$< 1 \times 10^{-15}$				
1028	$NO_3 + OCS \rightarrow$ products	$< 3 \times 10^{-15}$				
1029	$NO_3 + SO_2 \rightarrow$ products	$< 1 \times 10^{-19}$				
1029	$NO_3 + CH_3SH \rightarrow$ products	9.2×10^{-13}	±0.15	9.2×10^{-13}	250-370	±400
1030	$NO_3 + CH_3SCH_3 \rightarrow$ products	1.0×10^{-12}	±0.15	$1.9 \times 10^{-13}\exp(+500/T)$	250-380	±300
1031	$NO_3 + CH_3SSCH_3 \rightarrow$ products	7×10^{-13}	±0.3	7×10^{-13}	300-380	±500
***	$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3$	$< 5 \times 10^{-17}$				
	$\rightarrow CH_3O_2SO_2$	No recommendation (see data sheets)				
1032	$HS + O_2 \rightarrow HO + SO$	$\leq 4 \times 10^{-19}$				

Summary of Reactions and Preferred Rate Data -- Continued (21)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1032	$HS + O_3 \rightarrow HSO + O_2$	3.6×10^{-12}	±0.2			
1033	$HS + NO + M \rightarrow HSNO + M$	$2.4 \times 10^{-31}[N_2]$ (k_0)	±0.3	$2.4 \times 10^{-31}(T/300)^{-2.5}[N_2]$	200-300	$\Delta n = \pm 1$
		2.7×10^{-11} (k_∞)	±0.5	2.7×10^{-11}	200-300	
		$F_c = 0.6$				
1034	$HS + NO_2 \rightarrow HSO + NO$	5.8×10^{-11}	±0.3	$2.6 \times 10^{-11}\exp(+240/T)$	220-450	±200
1035	$HSO + O_2 \rightarrow$ products	$\leq 2 \times 10^{-17}$				
1035	$HSO + O_3 \rightarrow$ products	1.1×10^{-13}	±0.8			
1036	$HSO + NO \rightarrow$ products	$\leq 1 \times 10^{-15}$				
1036	$HSO + NO_2 \rightarrow$ products	9.6×10^{-12}	±0.3			
1037	$HSO_2 + O_2 \rightarrow$ products	3×10^{-13}	±0.8			
***	$SO + O_2 \rightarrow SO_2 + O$	6.7×10^{-17}	±0.15	$1.4 \times 10^{-13}\exp(-2275/T)$	230-420	±500
***	$SO + O_3 \rightarrow SO_2 + O_2$	8.9×10^{-14}	±0.1	$4.5 \times 10^{-12}\exp(-1170/T)$	230-420	±150
1037	$SO + NO_2 \rightarrow SO_2 + NO$	1.4×10^{-11}	±0.1	1.4×10^{-11}	210-360	±100
*	$SO_3 + H_2O \rightarrow$ products	No recommendation (see data sheets)				
*	$CS + O_2 \rightarrow$ products	No recommendation (see data sheets)				
1038	$O_3 + CH_3SCH_3 \rightarrow$ products	$<1 \times 10^{-18}$				

Summary of Reactions and Preferred Rate Data -- Continued (22)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		Δlog k_{298}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	Δ(E/R)/ K
***	OCS + hν → products	See data sheets					
***	CS_2 + hν → products	See data sheets					
**	CH_3SSCH_3 + hν → products	See data sheets					
	<u>FO_x Reactions</u>						
*	O + FO → O_2 + F	5 x 10^{-11}		±0.5			
*	O + FO_2 → O_2 + FO	5 x 10^{-11}		±0.7			
*	$O(^1D)$ + HF → HO + F	1 x 10^{-10}		±0.5			
***	$O(^1D)$ + COF_2 → CO_2 + F_2	2.2 x 10^{-11}		±0.2			
	→ $O(^3P)$ + COF_2	5.2 x 10^{-11}		±0.2			
**	F + H_2 → HF + H	2.8 x 10^{-11}		±0.1	1.9 x 10^{-10}exp(-570/T)	190-770	±150
***	F + H_2O → HF + HO	1.1 x 10^{-11}		±0.5	4.2 x 10^{-11}exp(-400/T)	240-370	±200
1038	F + O_2 + M → FO_2 + M	4.3 x 10^{-33}[N_2]	(k_o)	±0.3	4.3 x 10^{-33}(T/300)$^{-1.4}$[N_2]	200-300	Δn = ±1
		3 x 10^{-11}	(k_∞)	±0.5	3 x 10^{-11}	200-300	Δn = ±1
		F_c = 0.85		ΔF_c = ±0.1	F_c = exp(-T/1850)	200-300	
1039	FO_2 + M → F + O_2 + M	2.2 x 10^{-17}[N_2]	(k_o/s^{-1})	±0.5	6.3 x 10^{-9}exp(-5800/T)[N_2]s^{-1}	200-400	±1000

Summary of Reactions and Preferred Rate Data -- Continued (23)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta \log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
*	$F + O_3 \rightarrow FO + O_2$	1.3×10^{-11}	±0.3	$2.8 \times 10^{-11} \exp(-226/T)$	250-365	±200
***	$F + NO_2 + M \rightarrow FONO + M$	$1.0 \times 10^{-30}[O_2]$ (k_0)	±0.5	$1.0 \times 10^{-30}(T/300)^{-2.0}[O_2]$	200-300	$\Delta n = \pm 1$
		$1.0 \times 10^{-30}[N_2]$ (k_0)	±0.5	$1.0 \times 10^{-30}(T/300)^{-2.0}[N_2]$	200-300	$\Delta n = \pm 1$
		2×10^{-10} (k_∞)	±0.8	2×10^{-10}	200-300	$\Delta n = \pm 1$
		$F_c = 0.6$	$\Delta F_c = \pm 0.2$	$F_c = \exp(-T/587)$	200-300	
***	$F + CH_4 \rightarrow HF + CH_3$	8.0×10^{-11}	±0.2	$3.0 \times 10^{-10} \exp(-400/T)$	250-450	±200
1039	$HO + CH_3CHF_2 \rightarrow$ products	3.4×10^{-14}	±0.2			
1040	$HO + CH_2FCF_3 \rightarrow H_2O + CHFCF_3$	8.4×10^{-15}	±0.2	$6.6 \times 10^{-13} \exp(-1300/T)$	250-440	±300
*	$FO + O_3 \rightarrow$ products	No recommendation (see data sheets)				
**	$FO + NO \rightarrow F + NO_2$	2.6×10^{-11}	±0.3			
*	$FO + NO_2 + M \rightarrow FONO_2 + M$	$1.6 \times 10^{-31}[O_2]$ (k_0)	±0.7	$1.6 \times 10^{-31}(T/300)^{-3.4}[O_2]$	200-300	$\Delta n = \pm 1.0$
		$1.6 \times 10^{-31}[N_2]$ (k_0)	±0.7	$1.6 \times 10^{-31}(T/300)^{-3.4}[N_2]$	200-300	$\Delta n = \pm 1.0$
		2×10^{-11} (k_∞)	±0.5	2×10^{-11}	200-300	$\Delta n = \pm 0.5$
		$F_c = 0.5$	$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/433)$	200-300	
*	$FO + FO \rightarrow$ products	1.5×10^{-11}	±0.3			
**	$HF + h\nu \rightarrow$ products	See data sheets				

Summary of Reactions and Preferred Rate Data -- Continued (24)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta \log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
**	$FONO_2 + h\nu \rightarrow$ products	See data sheets				
***	$COF_2 + h\nu \rightarrow$ products	See data sheets				
	<u>ClO_x Reactions</u>					
***	$O + HCl \rightarrow HO + Cl$	1.4×10^{-16}	±0.3	$1.0 \times 10^{-11}\exp(-3340/T)$	293-718	±350
1041	$O + HOCl \rightarrow HO + ClO$	No recommendation (see data sheets)				
1041	$O + ClO \rightarrow O_2 + Cl$	3.8×10^{-11}	±0.1	3.8×10^{-11}	200-300	±250
1042	$O + OClO \rightarrow O_2 + ClO$	5×10^{-13}	±0.5			
	$\rightarrow O + ClOO$					
*	$O + ClONO_2 \rightarrow$ products	1.9×10^{-13}	±0.1	$3.0 \times 10^{-12}\exp(-808/T)$	213-295	±200
**	$O(^1D) + CF_2Cl_2 \rightarrow$ products	1.4×10^{-10}	±0.1			
**	$O(^1D) + CFCl_3 \rightarrow$ products	2.3×10^{-10}	±0.1			
**	$O(^1D) + CCl_4 \rightarrow$ products	3.3×10^{-10}	±0.1			
***	$Cl + H_2 \rightarrow HCl + H$	1.6×10^{-14}	±0.1	$3.7 \times 10^{-11}\exp(-2300/T)$	200-300	±200
1043	$Cl + HO_2 \rightarrow HCl + O_2$	3.2×10^{-11}	±0.2	$1.8 \times 10^{-11}\exp(+170/T)$	250-420	±250
	$\rightarrow ClO + HO$	9.1×10^{-12}	±0.3	$4.1 \times 10^{-11}\exp(-450/T)$	250-420	±250
*	$Cl + H_2O_2 \rightarrow HCl + HO_2$	4.3×10^{-13}	±0.2	$1.1 \times 10^{-11}\exp(-980/T)$	265-424	±500

Summary of Reactions and Preferred Rate Data -- Continued (25)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1043	$Cl + O_2 + M \rightarrow ClOO + M$	$1.7 \times 10^{-33}[N_2]$	±0.3			
1044	$ClOO + M \rightarrow Cl + O_2 + M$	$2.5 \times 10^{-13}[N_2]$ (k/s^{-1})	±0.5	$1.5 \times 10^{-8}\exp(-3285/T)[N_2]s^{-1}$	200-300	±1250
1044	$Cl + O_3 \rightarrow ClO + O_2$	1.2×10^{-11}	±0.06	$2.7 \times 10^{-11}\exp(-257/T)$	205-298	±100
1045	$Cl + HONO_2 \rightarrow HCl + NO_3$	$<2.0 \times 10^{-16}$				
1045	$Cl + NO_3 \rightarrow ClO + NO_2$	2.6×10^{-11}	±0.3	2.6×10^{-11}	200-300	±400
**	$Cl + CH_4 \rightarrow HCl + CH_3$	1.0×10^{-13}	±0.1	$9.6 \times 10^{-12}\exp(-1350/T)$	200-300	±250
*	$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	5.7×10^{-11}	±0.06	$7.7 \times 10^{-11}\exp(-90/T)$	220-350	±100
1046	$Cl + C_3H_8 \rightarrow HCl + C_3H_7$	1.5×10^{-10}	±0.2	$1.3 \times 10^{-10}\exp(+40/T)$	220-600	±200
***	$Cl + HCHO \rightarrow HCl + HCO$	7.3×10^{-11}	±0.06	$8.2 \times 10^{-11}\exp(-34/T)$	200-500	±100
1047	$Cl + CH_3CHO \rightarrow HCl + CH_3CO$	7.6×10^{-11}	±0.3			
1047	$Cl + CH_3CN \rightarrow$ products	$\leq 2 \times 10^{-15}$				
1048	$Cl + OClO \rightarrow 2\ ClO$	5.8×10^{-11}	±0.1	$3.4 \times 10^{-11}\exp(+160/T)$	298-450	±200
***	$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$	1.2×10^{-11}	±0.12	$6.8 \times 10^{-12}\exp(+160/T)$	219-298	±200
*	$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$	4.9×10^{-13}	±0.1	$3.4 \times 10^{-11}\exp(-1260/T)$	233-350	±200
***	$Cl + CH_3CCl_3 \rightarrow HCl + CH_2CCl_3$	$<4 \times 10^{-14}$	±0.1			
1049	$HO + HCl \rightarrow H_2O + Cl$	8.1×10^{-13}	±0.1	$2.4 \times 10^{-12}\exp(-330/T)$	200-300	±150
1050	$HO + HOCl \rightarrow H_2O + ClO$	5.0×10^{-13}	±0.5	$3.0 \times 10^{-12}\exp(-500/T)$	200-300	±500

Summary of Reactions and Preferred Rate Data -- Continued (26)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1050	$HO + ClO \rightarrow HO_2 + Cl$ $\rightarrow HCl + O_2$	1.7×10^{-11}	±0.2	$1.1 \times 10^{-11}\exp(+120/T)$	200-373	±150
1051	$HO + OClO \rightarrow HOCl + O_2$	7.0×10^{-12}	±0.3	$4.5 \times 10^{-13}\exp(+800/T)$	290-480	±200
*	$HO + ClONO_2 \rightarrow$ products	3.9×10^{-13}	±0.2	$1.2 \times 10^{-12}\exp(-330/T)$	246-387	±200
1052	$HO + CH_3Cl \rightarrow H_2O + CH_2Cl$	4.2×10^{-14}	±0.1	$1.9 \times 10^{-12}\exp(-1120/T)$	247-350	±200
1052	$HO + CH_2FCl \rightarrow H_2O + CHFCl$	4.4×10^{-14}	±0.1	$2.6 \times 10^{-12}\exp(-1210/T)$	245-350	±100
1052	$HO + CHF_2Cl \rightarrow H_2O + CF_2Cl$	4.7×10^{-15}	±0.1	$1.1 \times 10^{-12}\exp(-1620/T)$	250-360	±100
1052	$HO + CHFCl_2 \rightarrow H_2O + CFCl_2$	3.0×10^{-14}	±0.1	$1.1 \times 10^{-12}\exp(-1070/T)$	240-350	±100
1052	$HO + CH_2Cl_2 \rightarrow H_2O + CHCl_2$	1.4×10^{-13}	±0.1	$4.4 \times 10^{-12}\exp(-1030/T)$	240-300	±250
1053	$HO + CHCl_3 \rightarrow H_2O + CCl_3$	1.0×10^{-13}	±0.1	$3.3 \times 10^{-12}\exp(-1030/T)$	240-300	±100
1054	$HO + CFCl_3 \rightarrow HOCl + CFCl_2$	$<5 \times 10^{-18}$		$<1 \times 10^{-12}\exp(-3650/T)$	250-480	
1055	$HO + CF_2Cl_2 \rightarrow HOCl + CF_2Cl$	$<7 \times 10^{-18}$		$<1 \times 10^{-12}\exp(-3540/T)$	250-478	
1056	$HO + CCl_4 \rightarrow HOCl + CCl_3$	$<4 \times 10^{-16}$		$<1 \times 10^{-12}\exp(-2320/T)$		
1056	$HO + C_2HCl_3 \rightarrow$ products	2.2×10^{-12}	±0.1	$5.0 \times 10^{-13}\exp(+445/T)$	230-420	±200
1057	$HO + C_2Cl_4 \rightarrow$ products	1.7×10^{-13}	±0.1	$9.4 \times 10^{-12}\exp(-1200/T)$	300-420	±200
1058	$HO + CH_3CF_2Cl \rightarrow H_2O + CH_2CF_2Cl$	3.6×10^{-15}	±0.2	$1.6 \times 10^{-12}\exp(-1820/T)$	270-380	±300

Summary of Reactions and Preferred Rate Data -- Continued (27)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1058	$HO + CHFClCF_3 \rightarrow H_2O + CFClCF_3$	1.0×10^{-14}		±0.2	$6.4 \times 10^{-13}\exp(-1240/T)$	250-380	±300
1059	$HO + CH_2ClCF_2Cl \rightarrow H_2O + CHClCF_2Cl$	1.5×10^{-14}		±0.3	$3.0 \times 10^{-12}\exp(-1580/T)$	250-350	±500
1060	$HO + CHCl_2CF_3 \rightarrow H_2O + CCl_2CF_3$	3.4×10^{-14}		±0.2	$1.2 \times 10^{-12}\exp(-1060/T)$	245-375	±300
*	$HO + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$	1.2×10^{-14}		±0.15	$5.1 \times 10^{-12}\exp(-1800/T)$	250-460	±200
1060	$NO_3 + C_2HCl_3 \rightarrow$ products	2.9×10^{-16}		±0.3			
1061	$NO_3 + C_2Cl_4 \rightarrow$ products	$<1 \times 10^{-16}$					
1061	$ClO + HO_2 \rightarrow HOCl + O_2$	5.0×10^{-12}		±0.15	$4.6 \times 10^{-13}\exp(+710/T)$	200-300	±300
	$\rightarrow HCl + O_3$	$\leq 2 \times 10^{-14}$					
1062	$ClO + O_2(^1\Delta_g) \rightarrow$ sym-ClO_3	$<3.0 \times 10^{-15}$					
**	$ClO + NO \rightarrow Cl + NO_2$	1.7×10^{-11}		±0.1	$6.2 \times 10^{-12}\exp(+294/T)$	202-415	±100
1062	$ClO + NO_2 + M \rightarrow ClONO_2 + M$	$1.7 \times 10^{-31}[O_2]$	(k_o)	±0.1	$1.7 \times 10^{-31}(T/300)^{-3.4}[O_2]$	200-300	$\Delta n = \pm 1.0$
		$1.7 \times 10^{-31}[N_2]$	(k_o)	±0.1	$1.7 \times 10^{-31}(T/300)^{-3.4}[N_2]$	200-300	$\Delta n = \pm 1.0$
		2×10^{-11}	(k_∞)	±0.3	2×10^{-11}	200-300	$\Delta n = \pm 0.5$
		$F_c = 0.5$		$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/430)$		
1063	$ClO + NO_3 \rightarrow ClOO + NO_2$ $\rightarrow OClO + NO_2$	4.0×10^{-13}		±0.3			

Summary of Reactions and Preferred Rate Data -- Continued (28)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
**	$ClO + HCHO \rightarrow$ products	$<10^{-15}$					
1063	$ClO + ClO \rightarrow ClOO + Cl$	3.4×10^{-15}		±0.2			
	$\rightarrow OClO + Cl$	1.7×10^{-15}		±0.2			
	$\rightarrow Cl_2 + O_2$	4.9×10^{-15}		±0.2			
1065	$ClO + ClO + M \rightarrow Cl_2O_2 + M$	$4.0 \times 10^{-32}[N_2]$	(k_o)	±0.2	$4.0 \times 10^{-32}(T/300)^{-2.0}[N_2]$	200-300	$\Delta n = \pm1.0$
1066	$Cl_2O_2 + M \rightarrow ClO + ClO + M$	$6.1 \times 10^{-18}[N_2]$	(k_o/s^{-1})	±0.5	$3.1 \times 10^{-5}(T/300)^{-3} \times$ $\exp(-8720/T)[N_2]s^{-1}$	230-300	±500
1066	$OClO + NO \rightarrow ClO + NO_2$	3.4×10^{-13}		±0.3			
1067	$ClONO_2 + H_2O \rightarrow HOCl + HONO_2$	$<5.0 \times 10^{-21}$					
1067	$ClONO_2 + HCl \rightarrow Cl_2 + HONO_2$	$<2.0 \times 10^{-20}$					
1068	$CF_3 + O_2 + M \rightarrow CF_3O_2 + M$	$1.9 \times 10^{-29}[N_2]$	(k_o)	±0.2	$1.9 \times 10^{-29}(T/300)^{-4.7}[N_2]$	200-400	$\Delta n = \pm1$
		1×10^{-11}	(k_∞)	±0.2	1×10^{-11}	200-400	
		$F_c = 0.4$-0.5					
1069	$CFCl_2 + O_2 + M \rightarrow CFCl_2O_2 + M$	$5 \times 10^{-30}[N_2]$	(k_o)	±0.4	$5 \times 10^{-30}(T/300)^{-4}[N_2]$	200-300	$\Delta n = \pm2$
		6×10^{-12}	(k_∞)	±0.5	6×10^{-12}	200-300	
		$F_c = 0.6$					

Summary of Reactions and Preferred Rate Data -- Continued (29)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	Δlog k_{298}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	Δ(E/R)/ K
1070	$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$	$1.5 \times 10^{-30}[N_2]$ (k_o)	±0.5	$1.5 \times 10^{-30}(T/300)^{-4}[N_2]$	200-300	Δn = ±2
		5×10^{-12} (k_∞)	±0.3	5×10^{-12}	200-300	
		$F_c = 0.25$				
1071	$CCl_3O \rightarrow CCl_2O + Cl$	$>1 \times 10^{5}$ s^{-1} (233 K and 7.5 Torr)				
1071	$CCl_2FO \rightarrow CClFO + Cl$	$>3 \times 10^{4}$ s^{-1} (253 K and 6.7 Torr)				
1072	$CF_3O_2 + NO \rightarrow CF_3O + NO_2$	1.6×10^{-11}	±0.2	$1.6 \times 10^{-11}(T/300)^{-1.2}$	230-430	
1072	$CF_2ClO_2 + NO \rightarrow CF_2ClO + NO_2$	1.6×10^{-11}	±0.3	$1.6 \times 10^{-11}(T/300)^{-1.5}$	230-430	
1072	$CFCl_2O_2 + NO \rightarrow CFCl_2O + NO_2$	1.5×10^{-11}	±0.2	$1.5 \times 10^{-11}(T/300)^{-1.3}$	230-430	
1072	$CCl_3O_2 + NO \rightarrow CCl_3O + NO_2$	1.8×10^{-11}	±0.2	$1.8 \times 10^{-11}(T/300)^{-1.0}$	230-430	
1073	$CF_3O_2 + NO_2 + M \rightarrow CF_3O_2NO_2 + M$	$2.7 \times 10^{-29}[N_2]$ (k_o)	±0.3	$2.7 \times 10^{-29}(T/300)^{-5}[N_2]$	200-300	Δn = ±2
		9×10^{-12} (k_∞)	±0.5	$9 \times 10^{-12}(T/300)^{-0.7}$	200-300	Δn = ±1
		$F_c = 0.49$		$F_c = \exp(-T/416)$		
1074	$CF_2ClO_2 + NO_2 + M \rightarrow CF_2ClO_2NO_2 + M$	$4.0 \times 10^{-29}[N_2]$ (k_o)	±0.4	$4.0 \times 10^{-29}(T/300)^{-5}[N_2]$	200-300	Δn = ±2
		1.0×10^{-11} (k_∞)	±0.5	$1.0 \times 10^{-11}(T/300)^{-0.7}$	200-300	Δn = ±1
		$F_c = 0.45$		$F_c = \exp(-T/373)$		

Summary of Reactions and Preferred Rate Data -- Continued (30)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1074	$CF_2ClO_2NO_2 + M \rightarrow CF_2ClO_2 + NO_2 + M$	$1.5 \times 10^{-17}[N_2]$	(k_0/s^{-1})	±0.3	$5.6 \times 10^{-4}\exp(-9310/T)[N_2]s^{-1}$	260-290	±1000
		4.9×10^{-2}	(k_∞/s^{-1})	±0.3	$1.0 \times 10^{16}\exp(-11880/T)s^{-1}$	260-290	±1000
		$F_c = 0.4$					
1075	$CFCl_2O_2 + NO_2 + M \rightarrow CFCl_2O_2NO_2 + M$	$5.5 \times 10^{-29}[N_2]$	(k_0)	±0.3	$5.5 \times 10^{-29}(T/300)^{-5}[N_2]$	200-300	$\Delta n = \pm 1$
		8.3×10^{-12}	(k_∞)	±0.3	$8.3 \times 10^{-12}(T/300)^{-0.7}$	200-300	$\Delta n = \pm 1$
		$F_c = 0.42$			$F_c = \exp(-T/342)$		
1076	$CFCl_2O_2NO_2 + M \rightarrow CFCl_2O_2 + NO_2 + M$	$1.2 \times 10^{-18}[N_2]$	(k_0/s^{-1})	±0.3	$3 \times 10^{-3}\exp(-10570/T)[N_2]s^{-1}$	270-290	±1000
		7.3×10^{-2}	(k_∞/s^{-1})	±0.3	$2.1 \times 10^{16}\exp(-11980/T)s^{-1}$	270-290	±1000
		$F_c = 0.4$			$F_c = \exp(-T/342)$		
1077	$CCl_3O_2 + NO_2 + M \rightarrow CCl_3O_2NO_2 + M$	$9.2 \times 10^{-29}[N_2]$	(k_0)	±0.3	$9.2 \times 10^{-29}(T/300)^{-6}[N_2]$	200-300	$\Delta n = \pm 2$
		1.5×10^{-11}	(k_∞)	±0.3	$1.5 \times 10^{-11}(T/300)^{-0.3}$	200-300	$\Delta n = \pm 1$
		$F_c = 0.32$			$F_c = \exp(-T/260)$		
1078	$CCl_3O_2NO_2 + M \rightarrow CCl_3O_2 + NO_2 + M$	$1.5 \times 10^{-17}[N_2]$	(k_0/s^{-1})	±0.3	$5.6 \times 10^{-4}\exp(-9310/T)[N_2]s^{-1}$	260-300	±1000
		1.6×10^{-1}	(k_∞/s^{-1})	±0.3	$9.1 \times 10^{14}\exp(-10820/T)s^{-1}$	260-300	±1000
		$F_c = 0.20$					
1079	$CH_2ClO_2NO_2 + M \rightarrow CH_2ClO_2 + NO_2 + M$	See data sheets					

Summary of Reactions and Preferred Rate Data -- Continued (31)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1079	$O_3 + C_2HCl_3 \rightarrow$ products	$<5 \times 10^{-20}$				
1080	$O_3 + C_2Cl_4 \rightarrow$ products	$<10^{-21}$				
1080	$HOCl + h\nu \rightarrow$ products	See data sheets				
1081	$OClO + h\nu \rightarrow$ products	See data sheets				
1082	$Cl_2O_2 + h\nu \rightarrow$ products	See data sheets				
***	$ClONO_2 + h\nu \rightarrow$ products	See data sheets				
**	$COFCl + h\nu \rightarrow$ products	See data sheets				
**	$COCl_2 + h\nu \rightarrow$ products	See data sheets				
**	$CF_2Cl_2 + h\nu \rightarrow$ products	See data sheets				
**	$CFCl_3 + h\nu \rightarrow$ products	See data sheets				
**	$CCl_4 + h\nu \rightarrow$ products	See data sheets				
	<u>BrO_x Reactions</u>					
***	$O + HBr \rightarrow HO + Br$	3.7×10^{-14}	±0.12	$6.6 \times 10^{-12}\exp(-1540/T)$	220-455	±200
***	$O + Br_2 \rightarrow BrO + Br$	1.4×10^{-11}	±0.2			
*	$O + BrO \rightarrow O_2 + Br$	3×10^{-11}	±0.5			
1083	$Br + HO_2 \rightarrow HBr + O_2$	2.0×10^{-12}	±0.3	$1.4 \times 10^{-11}\exp(-590/T)$	260-390	±200

Summary of Reactions and Preferred Rate Data -- Continued (32)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1084	$Br + H_2O_2 \rightarrow HBr + HO_2$ $\rightarrow HOBr + HO$	<5 x 10^{-16}				
1084	$Br + O_3 \rightarrow BrO + O_2$	1.2 x 10^{-12}	±0.1	1.7 x 10^{-11}exp(-800/T)	220-360	±200
***	$Br + HCHO \rightarrow HBr + HCO$	1.0 x 10^{-12}	±0.15	1.7 x 10^{-11}exp(-800/T)	223-480	±250
1085	$Br + CH_3CHO \rightarrow HBr + CH_3CO$	3.6 x 10^{-12}	±0.2			
1086	$Br + OClO \rightarrow BrO + ClO$	3.4 x 10^{-13}	±0.3	2.6 x 10^{-11}exp(-1300/T)	200-450	±300
1086	$HO + HBr \rightarrow H_2O + Br$	1.1 x 10^{-11}	±0.1	1.1 x 10^{-11}	249-416	±250
1087	$HO + Br_2 \rightarrow HOBr + Br$	4.5 x 10^{-11}	±0.15	1.2 x 10^{-11}exp(+400/T)	260-360	±400
***	$HO + CH_3Br \rightarrow H_2O + CH_2Br$	3.8 x 10^{-14}	±0.1	7.6 x 10^{-13}exp(-890/T)	244-350	±200
***	$BrO + HO_2 \rightarrow HOBr + O_2$ $\rightarrow HBr + O_3$	5 x 10^{-12}	±0.5			
*	$BrO + O_3 \rightarrow Br + 2O_2$	<5 x 10^{-15}				
*	$BrO + NO \rightarrow Br + NO_2$	2.1 x 10^{-11}	±0.1	8.7 x 10^{-12}exp(+260/T)	224-425	±100
**	$BrO + NO_2 + M \rightarrow BrONO_2 + M$	5.0 x $10^{-31}[O_2]$ (k_0)	±0.3	5.0 x $10^{-31}(T/300)^{-3.0}[O_2]$	200-300	Δn = ±1
		5.0 x $10^{-31}[N_2]$ (k_0)	±0.3	5.0 x $10^{-31}(T/300)^{-3.0}[N_2]$	200-300	Δn = ±1
		2 x 10^{-11} (k_∞)	±0.3	2 x 10^{-11}	200-300	Δn = ±0.5
		$F_c = 0.4$	$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/327)$	200-300	

Summary of Reactions and Preferred Rate Data -- Continued (33)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1088	$BrO + ClO \rightarrow Br + OClO$	6.9×10^{-12}	±0.1	$1.9 \times 10^{-12}\exp(+390/T)$	200-400	±400
	$\rightarrow Br + ClOO$	6.4×10^{-12}	±0.1	$3.9 \times 10^{-12}\exp(+140/T)$	200-400	±200
	$\rightarrow BrCl + O_2$					
***	$BrO + BrO \rightarrow 2Br + O_2$	2.2×10^{-12}	±0.1	$1.1 \times 10^{-12}\exp(+255/T)$	223-398	±300
	$\rightarrow Br_2 + O_2$	4.5×10^{-13}	±0.2			
**	$HOBr + h\nu \rightarrow$ products	See data sheets				
1089	$BrO + h\nu \rightarrow$ products	See data sheets				
**	$BrONO_2 + h\nu \rightarrow$ products	See data sheets				
	<u>IO_x Reactions</u>					
***	$O + I_2 \rightarrow IO + I$	1.4×10^{-10}	±0.3	1.4×10^{-10}	200-400	±250
**	$O + IO \rightarrow O_2 + I$	5×10^{-11}	±0.5			
**	$I + HO_2 \rightarrow HI + O_2$	No recommendation (see data sheets)				
1090	$I + O_3 \rightarrow IO + O_2$	9.5×10^{-13}	±0.2			
**	$I + NO + M \rightarrow INO + M$	$1.8 \times 10^{-32}[O_2]$ (k_o)	±0.2	$1.8 \times 10^{-32}(T/300)^{-1.0}[O_2]$	200-300	Δn = ±0.5
		$1.8 \times 10^{-32}[N_2]$ (k_o)	±0.1	$1.8 \times 10^{-32}(T/300)^{-1.0}[N_2]$	200-300	Δn = ±0.5

Summary of Reactions and Preferred Rate Data -- Continued (34)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
		1.7×10^{-11}	(k_∞)	±0.3	1.7×10^{-11}	200-300	$\Delta n = \pm0.5$
		$F_c = 0.75$		$\Delta F_c = \pm0.15$	$F_c = \exp(-T/1043)$		
**	$I + NO_2 + M \rightarrow INO_2 + M$	$2.9 \times 10^{-31}[O_2]$	(k_0)	±0.3	$2.9 \times 10^{-31}(T/300)^{-1.0}[O_2]$	200-300	$\Delta n = \pm0.5$
		$2.9 \times 10^{-31}[N_2]$	(k_0)	±0.3	$2.9 \times 10^{-31}(T/300)^{-1.0}[N_2]$	200-300	$\Delta n = \pm0.5$
		6.6×10^{-11}	(k_∞)	±0.3	6.6×10^{-11}	200-300	$\Delta n = \pm0.5$
		$F_c = 0.63$		$\Delta F_c = \pm0.1$	$F_c = \exp(-T/650)$		
**	$HO + HI \rightarrow H_2O + I$	1.3×10^{-11}		±0.5			
1090	$HO + I_2 \rightarrow HOI + I$	1.8×10^{-10}		±0.3			
**	$IO + HO_2 \rightarrow$ products	No recommendation (see data sheets)					
1091	$IO + IO \rightarrow$ products	5.2×10^{-11}	(1 atm)	±0.5	$1.7 \times 10^{-12}\exp(+1020/T)$ (1 atm)	250-373	±200
**	$IO + NO \rightarrow I + NO_2$	1.7×10^{-11}		±0.3			
1092	$IO + NO_2 + M \rightarrow IONO_2 + M$	$3.4 \times 10^{-31}[O_2]$	(k_0)	±0.5	$3.4 \times 10^{-31}(T/300)^{-3.0}[O_2]$	200-400	$\Delta n = \pm1$
		$3.4 \times 10^{-31}[N_2]$	(k_0)	±0.5	$3.4 \times 10^{-31}(T/300)^{-3.0}[N_2]$	200-400	$\Delta n = \pm1$
		1.6×10^{-11}	(k_∞)	±0.5	1.6×10^{-11}	200-400	$\Delta n = \pm0.5$
		$F_c = 0.4$		$\Delta F_c = \pm0.1$	$F_c = \exp(-T/327)$		
1092	$IO + CH_3SCH_3 \rightarrow$ products	No recommendation (see data sheets)					

Summary of Reactions and Preferred Rate Data -- Continued (35)

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/ K
**	$INO + INO \rightarrow I_2 + 2\ NO$	1.3×10^{-14}	±0.4	$8.4 \times 10^{-11}\exp(-2620/T)$	298-450	±600
**	$INO_2 + INO_2 \rightarrow I_2 + 2\ NO_2$	4.7×10^{-15}	±0.5	$2.9 \times 10^{-11}\exp(-2600/T)$	298-400	±1000
**	$HOI + h\nu \rightarrow$ products	See data sheets				
1093	$IO + h\nu \rightarrow$ products	See data sheets				
**	$INO + h\nu \rightarrow$ products	See data sheets				
**	$INO_2 + h\nu \rightarrow$ products	See data sheets				
**	$IONO_2 + h\nu \rightarrow$ products	See data sheets				

*Data sheet for this reaction appears in earlier evaluation; J. Phys. Chem. Ref. Data **9**, 295 (1980).
Data sheet for this reaction appears in earlier evaluation; J. Phys. Chem. Ref. Data **11, 327 (1982).
***Data sheet for this reaction appears in earlier evaluation; J. Phys. Chem. Ref. Data **13**, 1259 (1984).

3. Guide to the Data Sheets

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

3.1. Thermal Reactions

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

The available kinetic data on the reactions are summarized under three headings: (i) Absolute Rate Coefficients, (ii) Relative Rate Coefficients, and (iii) Reviews and Evaluations. Under headings (i) and (ii), we list here only data which have been published since the previous CODATA evaluations,[1–3] and under heading (iii) are listed the preferred rate data from the most recent NASA evaluations,[4,5] from our own CODATA evaluation,[3] and from any new review or evaluation sources. Under all three of the headings above, the data are presented as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in a temperature-dependent form over a stated range of temperatures. For bimolecular reactions, the temperature dependence is usually expressed in the normal Arrhenius form, $k = A\exp(-C/T)$, where $C = E/R$. For a few bimolecular reactions, we have listed temperature dependences in the alternative form, $k = A'T^{-n}$ or $AT^{n}\exp(-C/T)$, 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 subsequent section of the introduction.

Single temperature data are presented as such and wherever possible the rate coefficient at 298 K is quoted directly as measured by the original authors. This means that the listed rate coefficient at 298 K may differ slightly from that calculated from the Arrhenius parameters determined by the same authors. Rate coefficients at 298 K marked with an asterisk indicate that the value was calculated by extrapolation of a measured temperature range which did not include 298 K.

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

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

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

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

A new type of "Comment" data sheet has been introduced in the present evaluation. For a given reaction this summarizes any new relevant reported data or finding, but which does not alter our previous recommendations for the reaction and consequently does not warrant a completely rewritten data sheet.

3.2. Conventions Concerning Rate Coefficients

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

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

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

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.

3.3. Treatment of Combination and Dissociation Reactions

The rates of combination and the reverse dissociation reactions

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

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

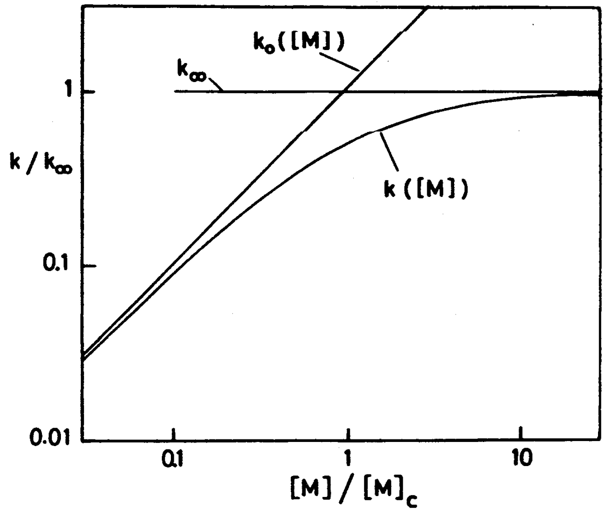

FIG. 1. Reduced fall-off curve of k/k_∞ as a function of $[M]/[M]_c$.

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

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

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

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

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

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

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

where the "center of the falloff curve" $[\mathrm{M}]_c$ indicates the third-body concentration for which the extrapolated k_0 would be equal to k_∞. This is illustrated in Fig.1. The dependence of k on [M] in general is complicated and has to be analyzed by unimolecular rate theory. For moderately complex molecules at not too high temperatures, however, a simple approximate relationship holds:

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

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

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

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

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

characterize the falloff curve for the present application.

Alternatively, the three quantities k_∞, $[\mathrm{M}]_c$, and F_c (or k_0, $[\mathrm{M}]_c$, and F_c) can be used. The temperature dependence of F_c, which is sometimes significant, can be estimated by the procedure of Troe.[6–8] The results can usually be represented[8] approximately by an equation

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

Whereas the two first terms are of importance for atmospheric conditions, the last term in most cases becomes relevant only at much higher temperatures. In Ref. 2, for simplicity $a = 1$ and $T^{**} = 4T^{*}$ was adopted. If F_c values are available for one temperature only, we also follow this policy in the present evaluation. Often the term $\exp(-T^{**}/T)$ is negligible at temperatures below 300 K. More detailed representations, however, will require specification of a, T^{***}, T^{*}, and T^{**}. Theoretical predictions[6–8] of F_c have been derived from rigid RRKM-type models including weak collision effects. Systematic calculations of this type have been presented by Patrick and Golden[9] for reactions of atmospheric interest. It is debatable whether these calculations can be applied to radical recombination reactions without barriers, where rotational effects are important. Changes in F_c would require changes in the limiting k_0 and k_∞ values. For the purpose of this evaluation, this will be irrelevant in most cases, if the preferred k_0 and k_∞ are used consistently together with the preferred F_c values.

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

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

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

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

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

3.4. 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 I. Calculated threshold wavelengths corresponding to these enthalpy changes are also listed.

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

The next table lists the preferred absorption cross-section data and the preferred quantum yields at wavelength intervals of 5 nm where possible. The preferred data are often amplified by diagrams of absorption cross sections versus wavelength and, where appropriate, by diagrams of quantum yield versus wavelength.

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

This evaluation contains data sheets only for photochemical reactions for which new data have been published since September 1983. Consequently for many of the photochemical reactions listed in the Summary of Reactions, it is necessary to refer back to our previous evaluations[1–3] for the corresponding detailed data sheets.

3.5. Conventions Concerning Absorption Cross Sections

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

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

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

3.6. Assignment of Errors

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

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

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

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

Acknowledgments

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4. Data Sheets

4.1. Oxygen Species

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

$\Delta H^\circ = -106.5$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.0\times10^{-33}(T/100)^{-3.2\pm0.3}$ [Ar]	80–150	Rawlins, Caledonia and Armstrong, 1987[1]	(a)
Reviews and Evaluations			
$6.2\times10^{-34}(T/300)^{-2.0}$ [O_2]	200–300	CODATA, 1984[2]	(b)
$5.7\times10^{-34}(T/300)^{-2.8}$ [N_2]	200–300		
$6.0\times10^{-34}(T/300)^{-2.3}$ [air]	200–300	NASA; 1987[3]	(c)

Comments

(a) Cold chemiexcitation infrared stimulation experiments. Microwave discharge of O_2/Ar mixtures at 1 Torr in a flow system. Observation of IR fluorescence near 10 μm from vibrationally excited O_3(v). Reactions of O_3(v) with O to form $2O_2$ have rate coefficients in excess of 10^{-11} cm^3 molecule^{-1} s^{-1} increasing with v.

(b) Average of data by Lin and Leu,[4] Klais, Anderson, and Kurylo,[5] and Arnold and Comes.[6]

(c) Based on data by Lin and Leu,[4] and Klais, Anderson, and Kurylo.[5]

Preferred Values

$k_0 = 6.2\times10^{-34}(T/300)^{-2.0}$ [O_2] cm^3 molecule^{-1} s^{-1} over range 200–300 K.

$k_0 = 5.7\times10^{-34}(T/300)^{-2.8}$ [N_2] cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The new low temperature data considerably extend the available temperature range. They extrapolate within the experimental uncertainties to the earlier room temperature results in Ar from Refs. 4–6. Although the new experiments have not changed our recommendation, they may provide evidence for an increase of the negative T exponent of k_0 with decreasing temperature. They also indicate preferential formation of vibrationally excited O_3 molecules during the recombination with excitation in the asymmetric stretching mode.

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$$O + O_2 \rightarrow O_3^{**} \tag{1}$$

$$O_3^{**} + M \rightarrow O_3^{*} + M \tag{2}$$

$$O_3^{*} + O \rightarrow 2O_2 \tag{3}$$

$$O_3^{*} + O_2(^1\Delta_g) \rightarrow 2O_2 + O \tag{4}$$

$$O_3^{*} + O_2(^1\Sigma_g^+) \rightarrow 2O_2 + O \tag{5}$$

Comments

By a detailed analysis[1] of IR fluorescence near 10 μm from vibrationally excited O_3, Rawlins, Caledonia, and Armstrong[2] have provided estimates of the rates of reactions (1)–(5) under low temperature conditions. The corresponding overall recombination rate coefficients for O_3 formation via the reaction $O + O_2 + M \rightarrow O_3 + M$ in the temperature range 80–150 K have been given in a separate data sheet in this evaluation.

References

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

Comments

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

References

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

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

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	M	Temp./K	Reference	Comments
Absolute Rate Coefficients				
$(3.3 \pm 0.4) \times 10^{-19}$	O_2	298	Eisenberg *et al.*, 1984[1]	(a)
$(1.65 \pm 0.07) \times 10^{-18}$	O_2	298	Raja, Arora, and Chatha, 1986[2]	(b)
$(3.15 \pm 0.1) \times 10^{-18} \exp(-205/T)$	O_2	100–450	Billington and Borrell, 1986[3]	(c)
1.57×10^{-18}	O_2	298		
$<0.5 \times 10^{-18}$	CO_2	298	Singh *et al.*, 1985[4]	(d)
Reviews and Evaluations				
1.7×10^{-18}	O_2	298	CODATA, 1984[5]	(e)
$\leqslant 1.4 \times 10^{-19}$	N_2			(f)
5×10^{-18}	H_2O			(g)
$\leqslant 2 \times 10^{-20}$	CO_2			(h)

Comments

(a) Direct laser excitation of O_2 at 1065 nm to give $O_2(^1\Delta g, v = 1)$. $O_2(^1\Delta g)$ was observed in emission at 1270 nm. Pressure was 1 atm O_2.

(b) Discharge flow system. $O_2(^1\Delta)$ monitored by dimol emission at 635 nm. Total pressure was 5–12 Torr.

(c) Discharge flow system. $O_2(^1\Delta)$ monitored by dimol emission at 634 nm and also by monitoring emission from $O_2(^1\Sigma_g^+)$ at 762 nm. Total pressure was 3–12 Torr.

(d) Discharge flow system. $O_2(^1\Delta)$ monitored in emission at 1270 nm. No quenching could be observed for $M = CO_2$.

(e) Based on Borrell *et al.*,[6] Leiss *et al.*,[7] and Findlay and Snelling.[8]

(f) Based on Hampson,[8] and Collins *et al.*[10]

(g) Based on Findlay and Snelling,[8] and Becker *et al.*[11]

(h) Based on Leiss *et al.*,[7] and Findlay and Snelling.[8]

Preferred Values

$k = 1.6 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} $M = O_2$ at 298 K.

$k = 3.0 \times 10^{-18} \exp(-200/T)$ cm^3 $molecule^{-1}$ s^{-1} for $M = O_2$ over range 100–450 K.

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

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

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

Reliability

$\Delta \log k = \pm 0.2$ for $M = O_2$ at 298 K.

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

$\Delta (E/R) = \pm 200$ K for $M = O_2$.

Comments on Preferred Values

The preferred value of $k(M = O_2)$ is based on the results of Raja *et al.*,[2] Billington and Borrell,[3] Borrell *et al.*,[6] and Leiss *et al.*[7] The temperature dependence of Billington and Borrell[3] is adopted in this evaluation. The much lower value of Eisenberg *et al.*[1] by a new technique is not used in derivation of the preferred value. The previous CODATA recommendation[5] for $M = N_2$, H_2O, and CO_2 are unchanged.

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

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

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	M	Temp./K	Reference	Comments
Absolute Rate Coefficients				
$(1.7 \pm 0.1) \times 10^{-15}$	N_2	298	Choo and Leu, 1985[1]	(a)
$(4.6 \pm 0.5) \times 10^{-13}$	CO_2	245-362	Choo and Leu, 1985[1]	(a)
$(3.47 \pm 0.46) \times 10^{-13}$	CO_2	295	Boodaghians, Borrell, and Borrell, 1983[2]	(b)
$(3.0 \pm 1.0) \times 10^{-13}$	CO_2	300	Singh and Setser, 1985[3]	(b)
Reviews and Evaluations				
4.0×10^{-17}	O_2	298	CODATA, 1984[4]	(c)
2.0×10^{-15}	N_2			(d)
8.0×10^{-14}	O			(e)
4.0×10^{-12}	H_2O			(f)
4.1×10^{-13}	CO_2			(g)

Comments

(a) Flow discharge-optical emission technique. $O_2(^1\Sigma_g^+)$ monitored in emission at 762 nm. Negligible temperature dependence observed for quenching by CO_2 over range 245–362 K with $E/R < 0 \pm 200$ K.

(b) Discharge flow system. $O_2(^1\Sigma_g^+)$ monitored in emission at 762 nm.

(c) Based on Thomas and Thrush,[5] Martin *et al.*,[6] Lawton *et al.*,[7] and Chatha *et al.*[8]

(d) Based on Kohse-Hoinghaus and Stuhl,[9] Martin *et al.*,[6] and Chatha *et al.*[8]

(e) Value of Slanger and Black.[10]

(f) Value of Thomas and Thrush.[5]

(g) Based on results of Filseth *et al.*,[11] Noxon,[12] Davidson *et al.*,[13] Aviles *et al.*,[14] Muller and Houston,[15] and Borrell *et al.*[16]

Preferred Values

$k = 2.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} for $M = N_2$ over range 200–350 K.

$k = 4.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} for $M = O_2$ at 298 K.

$k = 8.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for $M = O$ at 298 K.

$k = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for $M = H_2O$ at 298 K.

$k = 4.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for $M = CO_2$ over range 245–360 K.

Reliability

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

$\Delta \log k = \pm 0.1$ for $M = N_2$, CO_2 at 298 K.

$\Delta (E/R) = \pm 200$ K for $M = N_2$, CO_2.

Comments on Preferred Values

The value of $k(M = N_2)$ reported by Choo and Leu[1] is in good agreement with the previous CODATA recommendation.[4] The value of $k(M = CO_2)$ obtained by Choo and Leu[1] and by Boodaghians *et al.*,[2] are in good agreement with the previous recommendation. The results of Choo and Leu provide the only measurements over a range of temperatures, and the temperature independence reported is adopted in this evaluation. The other recommendations are also unchanged from our previous evaluation.[4]

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

$\Delta H^\circ(1) = -50.4$ kJ mol^{-1}
$\Delta H^\circ(2) = -62.6$ kJ mol^{-1}
$\Delta H^\circ(3) = -156.9$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.3) \times 10^{-11}$	295–361	Choo and Leu, 1985[1]	(a)
Reviews and Evaluations			
2.2×10^{-11}	298	CODATA, 1984[2]	(b)

Comments

(a) Flow discharge-optical emission technique. $O_2(^1\Sigma_g^+)$ monitored in emission at 762 nm. Negligible temperature dependence observed with $E/R < 0 \pm 300$ K.

(b) Based on data of Gilpin *et al.*, Snelling,[4] Slanger and Black,[5] Amimoto and Wiesenfeld,[6] and Ogren *et al.*[7]

Preferred Values

$k = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 295–360 K.

$k_1 = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta \log k_1 = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The recent study of Choo and Leu is in excellent agreement with the previous CODATA recommendation[2] which was only for room temperature. The new study covers the temperature range 295–360 K, and the temperature independence reported is adopted in the evaluation.

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$O_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH_0° /kJ mol^{-1}	λ threshold/nm
$O_2 + h\nu \rightarrow O(^3P) + O(^3P)$	494	242
$\rightarrow O(^3P) + O(^1D)$	683	175
$\rightarrow O(^1D) + O(^1D)$	873	137
$\rightarrow O(^3P) + O(^1S)$	898	132

Absorption cross section data

Wavelength range/nm	References	Comment
179–198	Yoshino *et al.*, 1987[1]	(a)
179–201	Yoshino *et al.*, 1983[2]	(b)
175–205	Yoshino, Freeman, and Parkinson, 1984[3]	(c)
193–204	Cheung *et al.*, 1984[4]	(d)
205–241	Cheung *et al.*, 1986[5]	(e)
205–225	Johnston, Paige, and Yao, 1984[6]	(f)
205–240	Jenouvrier, Coquart, and Merienne, 1986[7]	(g)
175–247	WMO, 1985[8]	(h)
175–205	Nicolet, Cieslik, and Kennes, 1987[9]	(i)

Comments

(a) Measured at 79 K with spectral resolution of 0.0013 nm. Band oscillator strengths of *S–R* bands (12, 0) through (2, 0) determined by numerical integration of cross section data.

(b) Measured at 300 K with spectral resolution 0.0013 nm. Band oscillator strengths of *S–R* band (12, 0) through (1, 0) determined.

(c) Measured at 300 K at high resolution with vacuum spectrograph. Includes an atlas of *S–R* absorption bands of O_2 at 300 K showing detailed rotation line assignments for 175–205 nm region.

(d) Measured at 300 K with spectral resolution of 0.0013 nm. Absorption includes discrete line of *S–R* bands and two underlying dissociation continua— the weak Herzberg continuum of O_2 and a pressure-dependent continuum involving two oxygen molecules.

(e) Measured at 296–300 K with spectral resolution of 0.13 nm and O_2 pressures of 5–760 Torr. Observed attenuation due to Rayleigh scattering and to absorption into two continua [see note (d)].

(f) Measured at 206–327 K with spectral resolution of 0.2 nm and O_2 pressures of 100–750 Torr.

(g) Measured at 289–294 K at low spectral resolution and O_2 pressures of 5–100 Torr.

(h) Critical review of all published data. Recommended values given for standard spectral intervals from 175–247 nm. Transmission in the *S–R* system (bands + continuum) tabulated as a function of column O_2 for standard spectral intervals from 175–206 nm.

(i) Tables of calculated absorption cross sections presented for the range of the (0, 0) to (19, 0) bands from 49 000 to 57 000 cm^{-1} and the temperature range 190–300 K in 32 intervals of 250 cm^{-1}.

Preferred Values

Absorption cross section of O_2 in the Herzberg continuum

λ/nm	$\sigma/10^{-24}$ cm^2
195	6.26
200	6.59
205	6.50
210	5.89
215	5.04
220	3.94
225	3.00
230	2.07
235	1.40
240	0.96

Comments on Preferred Values

The recommended absorption cross section values for the Herzberg continuum are taken from the recent study by Cheung *et al.*,[5] where values are tabulated for every nm from 195–241 nm. They are in agreement with the results of Johnston *et al.*[6] and are in reasonable agreement with the slightly higher results of Jenouvrier *et al.*[7] They are consistent with the lower absorption cross-section values inferred from balloon-borne measurements of solar irradiance attenuation in the stratosphere by Frederick and Mentall,[10] by Herman and Mentall,[11] and by Anderson and Hall,[12] but are in disagreement with the results derived by Pirre *et al.*,[13] from a similar *in situ* stratospheric study. An analysis of the photodissociation of oxygen in the Herzberg continuum has recently been published by Nicolet and Kennes.[14]

For the Schumann–Runge wavelength region the reader is referred to the review in WMO, 1985[8] and to the tables of absorption cross sections in Nicolet *et al.*[9] In this spectral region a detailed analysis of the penetration of solar radiation requires absorption cross-section measurements with very high spectral resolution. Absorption cross-section values for the (0, 0)–(12, 0) *S–R* bands measured by the Harvard–Smithsonian group[1–4] are the first set of values which are independent of instrumental width. Band oscillator strengths for these bands have been determined by direct numerical integration of these absolute cross-section values.

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$O_3 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_0/kJ mol^{-1}	λ threshold/nm
$O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Sigma_g^-)$	(1)	101	1180
$\rightarrow O(^3P) + O_2(^1\Delta_g)$	(2)	196	611
$\rightarrow O(^3P) + O_2(^1\Sigma_g^+)$	(3)	258	463
$\rightarrow O(^1D) + O_2(^3\Sigma_g^-)$	(4)	291	411
$\rightarrow O(^1D) + O_2(^1\Delta_g)$	(5)	386	310
$\rightarrow O(^1D) + O_2(^1\Sigma_g^+)$	(6)	448	267

Absorption cross section data

Wavelength range/nm	References	Comment
185–350	Molina and Molina, 1986[1]	(a)
245–350	Bass and Paur, 1985[2]	(b)
240–350	Freeman *et al.*, 1984[3]	(c)
238–335	Yoshino *et al.*, 1988[4]	(d)
310–350	Malicet, Brion, and Daumont, 1985[5]	(e)
254	Mauersberger *et al.*, 1986[6]	(f)
175–360	WMO, 1985[7]	(g)

Comments

(a) Measured at 226–298 K with spectral resolution of 0.07 nm.

(b) Measured at 200–300 K with spectral resolution of 0.025 nm. Relative values normalized to values of 1147×10^{-20} cm^2 at the 253.65 nm mercury line.

(c) Measured at 195 K with spectral resolution of 0.003 nm. Relative values normalized to values of five mercury lines.

(d) Measured at 195, 228, and 293 K at 13 wavelengths in this region. These absolute measurements were used to convert relative values in Ref. 3 to absolute values.

(e) Measured at 228 and 298 K at five mercury line wavelengths in the ultraviolet and in the continuous spectral range 320–330 nm with spectral resolution of 0.02 nm.

(f) Measured at 297 K at the 253.7 nm mercury line. Late measurements (Ref. 8) extended measurement to temperature range 195–351 K.

(g) Critical review of all published data. Recommended values given for standard spectral intervals from 175–360 nm for 203 and 273 K. Recommended values also tabulated for visible spectral region.

Ozone absorption cross sections at 273 K averaged over spectral internals

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

$\sigma = (1147 \pm 20)$ x 10^{-20} cm^2 at 253.7 nm

Ozone absorption cross sections in the visible spectral region

λ/nm	$10^{23}\sigma$/cm^2	λ/nm	$10^{23}\sigma$/cm^2
410	2.9	560	388
420	4.0	580	455
440	12.5	600	489
460	35.7	620	390
480	71.1	640	274
500	122	660	202
520	178	680	142
540	288	700	92

Quantum yields for O_3 photolysis

λ/nm	Quantum yield	T/K
248-300	$\phi_5 = 0.9 \pm 0.1$	200-300
248-300	$\phi_1 + \phi_5 = 1.00$	200-300
302	$\phi_5 = 0.90$	298
304	0.90	298
306	0.85	298
308	0.74	298
310	0.56	298
312	0.34	298
314	0.18	298
316	0.08	298
318	0.02	298
320	0.00	298

Comments on Preferred Values

Absorption cross sections

The recommended absorption cross section values for the wavelength range 175–362 nm are averaged values for the standard spectral intervals used in modeling calculations. These values have been adopted from the NASA 1987 review,[9] which accepted the values tabulated in the WMO 1985 review,[7] except for the region 185–225 nm where the values are taken from the recent study of Molina and Molina.[1] For the 245–350 nm region the results of Bass and Paur[2] are used, while for the remaining spectral regions the values were originally tabulated in Ackerman's review.[10] The value recommended for the mercury line at 253.7 nm is based on results reported by Hearn,[11] by Molina and Molina,[1] and by Mauersberger *et al.*[6] The values for the wavelength range 400–700 nm are taken from the WMO 1985 review.[7] The spectroscopy of ozone has been reviewed very recently by Steinfeld. Adler-Golden, and Gallagher.[16]

Quantum yields

The recommended quantum yield values for the 248–300 nm region are based on absolute quantum yield measurements at 248–266 nm (see CODATA 1984[12] and CODATA 1982[13]). The quantum yield values for 300–320 nm have been calculated from the expression for $\phi_5(\lambda,T)$ given in the NASA 1987 review.[9] That expression was derived from the expression of Mootgat and Kudszus[14] by using the scaling factor 0.9 to account for the absolute value of ϕ_5 at the shorter wavelengths. There is a need to confirm that the values of ϕ_5 determined at 248–266 nm applies throughout the wavelength region up to 300 nm (see review by Wayne[15]).

References

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

[2] A. M. Bass and R. J. Paur, "Atmospheric Ozone," in *Proceedings of Quadrennial Ozone Symposium in Halkidiki,* Greece (Reidel, Dordrecht, 1985), pp. 606–616.

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[6] K. Mauersberger, J. Barnes, D. Hanson, and J. Morton, Geophys. Res. Lett. **13**, 671 (1986).

[7] WMO Global Ozone Research and Monitoring Project Report No. 16, Atmospheric Ozone 1985, Chap. 7.

[8] J. Barnes and K. Mauersberger, J. Geophys. Res. **92**, 14861 (1987).

[9] NASA, 1987 (see References in Introduction).

[10] M. Ackerman, in *Mesospheric Models and Related Experiments* (Reidel, Dordrecht, 1971), pp. 149–159.

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

[12] CODATA, 1984 (see References in Introduction).

[13] CODATA, 1982 (see References in Introduction).

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

[15] R. P. Wayne, Atmos. Environ. **21**, 1683 (1987).

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

4.2. Hydrogen Species

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

$\Delta H^\circ(1) = -233 \text{ kJ mol}^{-1}$
$\Delta H^\circ(2) = -154 \text{ kJ mol}^{-1}$
$\Delta H^\circ(3) = -225 \text{ kJ mol}^{-1}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.7 \pm 1.5) \times 10^{-11}$	245–300	Keyser, 1986[1]	(a)
Branching Ratios			
$k_1/k = (0.08 \pm 0.04)$ $k_2/k = (0.90 \pm 0.04)$ $k_3/k = (0.02 \pm 0.04)$	245–300	Keyser, 1986[1]	(a)
Reviews and Evaluations			
7.4×10^{-11}	298	CODATA, 1984[2]	(b)
7.4×10^{-11}	200–300	NASA, 1985[3]	(b)
8.1×10^{-11}	200–300	NASA, 1987[4]	(c)

Comments

(a) Discharge flow system, He carrier gas. HO_2 in large excess over H. HO_2 produced by $F = H_2O_2$ reaction. $[HO_2]$ monitored by conversion to HO by reaction with NO, laser resonance fluorescence detection of HO. Reaction products, HO, O, detected by resonance fluorescence.

(b) Accepts value of Sridharan, Qui, and Kaufman.[5]

(c) Based on Sridharan *et al.*[5] and Keyser.[1]

Preferred Values

$k = 8.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 245–300 K.

$k_1 = 5.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the range 245–300 K.

$k_2 = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 245–300 K.

$k_3 = 2.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the range 245–300 K.

Reliability

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

Comments on Preferred Values

The recent study of Keyser[1] is the most detailed to date. Several species were monitored and the possible effects of side reactions were carefully analyzed. Values obtained for the overall rate coefficient and the branching ratios agree with the values obtained by Sridharan *et al.*[5] who used a similar technique. The recommended values for k and the branching ratios are the means of values from these two studies. In both cases k_1/k was not measured directly but obtained by difference. A direct measurement of this branching ratio is desirable.

Keyser *et al.*[6] have measured the yield of $O_2(b\ ^1\Sigma_g^+)$ to be $< 10^{-2}$ per HO_2 radical consumed.

Keyser[1] observed no effect of temperature change on k over the small range studied. This suggests that the value of $k_2 = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 349 K obtained by Pagsberg *et al.*[6] is too low or there is a substantial negative temperature coefficient. We provisionally recommend $E/R = 0$ but only over the range 245–300 K.

References

[1] L. F. Keyser, J. Phys. Chem. **90** 2994 (1986).

[2] CODATA Supplement II, 1984 (See References in Introduction).

[3] NASA Evaluation No. 7, 1985 (See References in Introduction).

[4] NASA Evaluation No. 8, 1987 (See References in Introduction).

[5] U. C. Sridharan, L. X. Qui, and F. Kaufman, J. Phys. Chem. **86**, 4569 (1982).

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[7] P. B. Pagsberg, J. Eriksen, and H. C. Christensen, J. Phys. Chem. **83**, 582 (1979).

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

$\Delta H^\circ = -203.1$ kJ mol^{-1}

Comment

Hsu, Durant, and Kaufman[1] have performed a discharge flow study with resonance fluorescence detection of H, HO, and HO_2 (by chemical titration) at 298 K and over the pressure range 4–30 Torr. The low-pressure rate coefficients $(2.6 \pm 0.2) \times 10^{-32}$ [He], $(6.1 \pm 0.9) \times 10^{-32}$ [N_2], and $(6.4 \pm 0.8) \times 10^{-31}$ [H_2O] cm^3 molecule^{-1} s^{-1} are in excellent agreement with our previous recommendation[2] which remains unaltered.

References

[1] K.-J. Hsu, J. L. Durant, and F. Kaufman, J. Phys. Chem. **91**, 1895 (1987).

[2] CODATA Supplement II, 1984 (See References in Introduction).

$H + O_3 \rightarrow HO^*(v = n) + O_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Branching Ratios			
$k_{v=6}/k = 0.04$	~298	Steinfeld, Adler-Golden, and Gallagher, 1987[1]	(a)
$k_{v=7}/k = 0.17$	~298		
$k_{v=8}/k = 0.35$	~298		
$k_{v=9}/k = 0.43$	~298		
Reviews and Evaluations			
$k_{v=3} = 2.0 \times 10^{-12}$	298	CODATA, 1984[2]	(b)
$k_{v=4} = 2.5 \times 10^{-12}$	298		
$k_{v=5} = 2.8 \times 10^{-12}$	298		
$k_{v=6} \leqslant 3.1 \times 10^{-12}$	298		
$k_{v=7} = 3.1 \times 10^{-12}$	298		
$k_{v=8} = 6.4 \times 10^{-12}$	298		
$k_{v=9} = 7.8 \times 10^{-12}$	298		

Comments

(a) HO infrared chemiluminescence data of Charters *et al.*[3] reanalyzed to correct for collisional quenching of higher vibrational states. Linear surprisal analysis used.

(b) Based on results of Charters *et al.*[3]

Preferred Values

$k_{v=6} = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=7} = 4.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=8} = 9.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=9} = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The previous CODATA recommendations were based on the results of Charters *et al.*[3] but it was assumed that their reported vibrational populations of HO corresponded to the nascent populations and hence ignored effects of collisional quenching of higher vibrational levels. Steinfeld *et al.* have reanalyzed the data using linear surprisal analysis to correct for the quenching. The new recommendations are based on their corrected values of the branching ratios together with the CODATA recommendation for the overall rate coefficient of $k = 2.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Values of $k_{v=5}$ to $k_{v=0}$ are extremely uncertain but contribute less than 1% to the overall k.

References

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

[2] CODATA Supplement II, 1984 (See References in Introduction).

[3] P. E. Charters, R. G. MacDonald, and J. C. Polanyi, Appl. Opt. **10**, 1747 (1971).

$O + H_2 \rightarrow HO + H$

$\Delta H^\circ = 8.1$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.25 \times 10^{-35} T^{7.8} \exp(-966/T)$	297–471	Presser and Gordon, 1985[1]	(a)
1.03×10^{-17}	297		
Reviews and Evaluations			
9×10^{-18}	298	CODATA, 1984[2]	(b)

Comments

(a) Flash photolysis of $O_2/Ar/H_2$ mixtures over total pressure range of 100–600 Torr. $[O(^3P)]$ monitored by resonance fluorescence at 130 nm. Rate coefficients for reaction of $O(^3P)$ with HD and D_2 also measured. Quoted expression is least squares fit to the 9 data points quoted.

(b) Accepts value of Light and Matsumoto.[3]

Preferred Value

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

Reliability

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

Comments on Preferred Values

In the only recent study Presser and Gordon obtain a value for k at 298 K in excellent agreement with the previous CODATA recommendation. This recommendation is therefore unchanged but the error limits are slightly reduced.

These new results tend to confirm that the Arrhenius plot is curved at temperatures below 400 K but the curvature may not be as pronounced as previous results suggest.

References

[1] N. Presser and R. J. Gordon, J. Chem. Phys. **82**, 1291 (1985).
[2] CODATA Supplement II, 1984 (See References in Introduction).
[3] G. C. Light and J. H. Matsumoto, Int. J. Chem. Kinet. **12**, 451 (1980).

$O + HO_2 \rightarrow HO + O_2$

$\Delta H^\circ = -225$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.91 \pm 0.70) \times 10^{-11} \exp[(228 \pm 75)/T]$	266–391	Nicovich and Wine, 1987[1]	(a)
$(6.30 \pm 0.91) \times 10^{-11}$	298		
Reviews and Evaluations			
$2.9 \times 10^{-11} \exp(200/T)$	200–400	CODATA, 1984[2]	(b)
$3.0 \times 10^{-11} \exp(200/T)$	200–300	NASA, 1985[3]	(c)
$3.0 \times 10^{-11} \exp(200/T)$	200–300	NASA, 1985[4]	(d)

Comments

(a) Pulsed laser photolysis of $H_2O_2/O_3/N_2$ mixtures at 248.5 nm. Total pressure 80 Torr. $[O(^3P)]$ monitored by resonance fluorescence.

(b) Based on results of Keyser,[5] Sridharan *et al.*,[6] Ravishankara *et al.*,[7] and Brune *et al.*[8]

(c) Based on results cited in (b).

(d) Based on results cited in (b) and those of Nicovich and Wine[1].

Preferred Values

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

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

Reliability

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

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

Comments on Preferred Values

The new study of Nicovich and Wine[1] is in excellent agreement with our previous recommendations for k which are unchanged but the error limits have been reduced.

There are also two new studies of the reaction mechanism. Keyer *et al.*[9] have shown that the yield of $O_2(b\,^1\Sigma_g^+)$ from the reaction is $< 1 \times 10^{-2}$ per HO_2 removed. Sridharan *et al.*[10] have shown in an ^{18}O labeling experiment that the reaction proceeds via formation of an HO_2–^{18}O intermediate which dissociates to OH and ^{18}OO by rupture of an O—O bond rather than via a four central intermediate yielding $^{18}OH + OO$.

References

[1] J. M. Nicovich and P. H. Wine, J. Phys. Chem. **91**, 5118 (1987).
[2] CODATA Supplement II, 1984 (See References in Introduction).
[3] NASA Evaluation No. 7, 1985 (See References in Introduction).
[4] NASA Evaluation No. 8, 1987 (See References in Introduction).
[5] L. F. Keyser, J. Phys. Chem. **86**, 8439 (1982).
[6] U. C. Sridharna, L. X. Qiu, and K. Kaufman, J. Phys. Chem. **86**, 459 (1982).
[7] A. R. Ravishankara, P. H. Wine, and J. M. Nicovich, J. Chem. Phys. Phys. **78**, 6629 (1983).
[8] Wm. H. Brune, J. J. Schwab, and J. G. Anderson, J. Phys. Chem. **87**, 4503 (1983).
[9] L. F. Keyser, K. Y. Choo, and M. T. Leu, Int. J. Chem. Kinet. **17**, 1169 (1985).
[11] U. C. Sridharan, F. S. Klein, and F. Kaufman, J. Chem. Phys. **82**, 592 (1985).

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

Comments

Glinski and Birks[1] have studied the branching ratios by gas chromatographic analysis of the products from photolysis at 253.7 nm of O_3/H_2O mixtures at total pressures of ~ 15 Torr. They find $k_2/k_1 < (0.006^{+0.007}_{-0.006})$.

References

[1] R. J. Glinski and J. W. Birks, J. Phys. Chem. **89**, 3449 (1985); J. Phys. Chem. **90**, 342 (1986) (Erratum).

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

$\Delta H° = -214.9$ kJ mol^{-1}

Comments

In a recent theoretical analysis of the unimolecular dissociation of H_2O_2 Brouwer *et al.*[1] have interpreted collision-free dissociation of H_2O_2 after overtone excitation and high pressure thermal recombination of HO radicals in a consistent way. The analysis of the available experimental data leads to $k_0 = 8 \times 10^{-31} (T/300)^{-0.76} [N_2]$ cm^3 molecule^{-1} s^{-1}, $k_\infty = 1.5 \times 10^{-11} (T/300)^{-0.37}$ cm^3 molecule^{-1} s^{-1}, and $F_C = 0.5$ over the range 200–1500 K. Although these values differ to some extent from our previous recommendation,[2] a change in the recommendation will be made only when new thermal experimental data are available which reduce the uncertainties ($\Delta \log k_0 = \pm 0.5$, $\Delta \log k_\infty = \pm 0.5$ at 300 K).

References

[1] L. Brouwer, C. J. Cobos, J. Troe, H.-R. Dübal, and F. F. Crim, J. Chem. Phys. **86**, 6171 (1987).
[2] CODATA Supplement II, 1984 (See References in Introduction).

$HO + HO_2 \rightarrow H_2O + O_2$

$\Delta H° = -296$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.2 \pm 1.2) \times 10^{-11}$	298	Rozenshtein *et al.*, 1984[1]	(a)
$(1.7 \pm 0.5) \times 10^{-11} \exp[416 \pm 86)/T]$	252–420	Sridharan, Qui, and Kaufman, 1984[2]	(b)
(2.5 Torr He)			
$(6.9 \pm 1.1) \times 10^{-11}$	298		
$(4.8 \pm 0.8) \times 10^{-11} \exp[250 \pm 50)/T]$	254–382	Keyser, 1988[3]	(c)
(1 Torr He)			
$(1.1 \pm 0.3) \times 10^{-10}$	299		
Reviews and Evaluations			
$(6.6 + 1.8 \times 10^{-19}[M]) \times 10^{-11}$	298	CODATA, 1984[4]	(d)
$1.7 \times 10^{-11} \exp(416/T)$ $+ 3.0 \times 10^{-31} \exp(500/T)[M]$	200–300	NASA, 1985[5]	(e)
$4.6 \times 10^{-11} \exp(230/T)$	200–300	NASA, 1987[6]	(f)

Comments

(a) Discharge-flow study, He carrier gas. HO_2 produced by $F + H_2O_2$ reaction, HO by reaction sequence $H + O_2 \rightarrow HO_2 + M$, $HO_2 + H \rightarrow HO + HO$. [HO] monitored by e.s.r., $[HO_2]$ by L.M.R.

(b) Discharge-flow study, He carrier gas. HO_2 produced by $H + F_2 \rightarrow HF + F$, $F + H_2O \rightarrow HF + HO$. [HO] monitored by laser induced fluorescence at 308.6 nm $[HO_2]$ detemined by rapid conversion to HO by reaction with NO and detection of HO by laser induced fluorescence $[HO_2]$ in large excess over [HO].

(c) Discharge-flow study, He carrier gas. HO_2 produced by $F + H_2O_2$ and OH by $F + H_2O$. Large excess of HO_2 used. [HO] monitored by resonance fluorescence and $[HO_2]$ determined by titration with NO. NO_2 added to system to scavenge small amounts of O and H present.

(d) Based on Sridharan *et al.*,[7] Kurylo *et al.*,[8] Temps and Wagner,[9] Thrush and Wilkinson,[10] Cox *et al.*,[11] DeMore,[12] Lii *et al.*,[13] Hochenadel *et al.*,[14] Burrows *et al.*,[15] Keyser,[16] Bruan *et al.*[17]

(e) Based on references cited in (d) plus Sridharan *et al.*[2] The temperature coefficient of the pressure-dependent term is estimated by analogy with that of the reaction $HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$.

(f) Based on Keyser.[3]

Preferred Values

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

$k = 4.8 \times 10^{-11} \exp(250/T)$ cm^3 molecule^{-1} s^{-1} over range 250–400 K.

Reliability

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

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

Comments on Preferred Values

There has been considerable controversy over the effects of pressure changes on the rate coefficient for this reaction. Previous discharge flow measurements at low pressures (1–10 Torr) have consistently given values of k approximately a factor of 2 lower than those obtained by other techniques at pressures close to atmospheric. The recent discharge-flow study of Keyser[3] appears to have resolved the problem. His results suggest that (a) the pressure of small quantities of H and O present in previous discharge-flow studies could have led to erroneously low values of k, and (b) there is no evidence for any variation in k with pressure. These findings are provisionally accepted in our recommendations as is his expression for k.

In another discharge-flow study Keyser *et al.*,[18] by monitored the $O_2(b\,\Sigma_g^+) \rightarrow X\,(^3\Sigma_g^-)$ transition at 762 nm, have shown that the yield of $O_2(b\,\Sigma_g^-)$ from the reaction is small ($< 1 \times 10^{-3}$).

References

[1] V. B. Rozenshtein, Y. M. Gershenzon, S. D. Il'in, and O. P. Kiskovitch, Chem. Phys. Lett. **112**, 473 (1984).

[2] U. C. Sridharan, L. X. Qui, and F. Kaufman, J. Phys. Chem. **88**, 1281 (1984).

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

[4] CODATA Supplement II, 1984 (See References in Introduction).

[5] NASA Evaluation No. 7, 1985 (See References in Introduction).

[6] NASA Evaluation No. 8, 1987 (See References in Introduction).

[7] U. C. Sridharan, L. X. Qui, and F. Kaufman, J. Phys. Chem. **85**, 3361 (1981).

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$HO + H_2O_2 \rightarrow H_2O + HO_2$

Comments

There is a flash photolysis-resonance fluorescence study by Lamb *et al.*[1] not tabulated in the previous CODATA compilation.[2] The results are in excellent agreement with the previous recommendations which are unchanged.

References

[1] T. Lamb, L. T. Molina, C. A. Smith, and M. J. Molina, J. Phys. Chem. **87**, 4467 (1983).

[2] CODATA Supplement II, 1984 (See References in Introduction).

$HO + O_3 \rightarrow HO_2 + O_2$

Comments

The only study since our last evaluation of this reaction is that of Smith *et al.*[1] in which HO was produced by flash photolysis of O_3–H_2O–He mixtures and the [HO] monitored by resonance fluorescence at 308 nm.

Experiments were conducted at 1 atm. He pressure and over the range 240–290 K. The expression for k derived is $k = (1.52 \pm 0.10) \times 10^{-12} \exp[(-890 \pm 60)/T]$ cm^3 molecule^{-1} s^{-1} in good agreement with our previous recommendations which are unchanged.[4]

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$HO^*(v=n)+O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_{v=9} \sim 2\times10^{-10}$	298	Greenblatt and Wiesenfeld, 1982[1]	(a)
Reviews and Evaluations			
$k_{v=9} = 9.4\times10^{-12}$	298	CODATA, 1984[2]	(b)

Comments

(a) Laser photolysis of $O_3/H_2/He$ mixtures at 248 nm. Decay of $[HO(v=9)]$ followed by observation of the $\Delta v = 6$ transition at 625 nm.

(b) Based on work of Streit and Johnston[3] and Coltharp *et al.*[4]

Preferred Values

No recommendation.

Comments on Preferred Values

The value of $k_{v=9}$ obtained by Greenblatt and Wiesenfled[1] is more than an order of magnitude greater than that of Streit and Johnston[3] on which our previous recommendation was based. This high value received some support from experiments by Slanger and Huestis[5] who passed mixtures of $O_3/H_2/He$ through a flow cell at 300 K and observed an abrupt generation of $O(^3P)$ at a critical O_3/H_2 ratio. The $[O(^3P)]$ profile was monitored by resonance fluorescence. Computer modelling of the profile showed that to obtain a good match with experiment it was necessary to use a value of $k_{v=0}$ comparable with that of Greenblatt and Wiesenfeld[1] and the value of $k_{v=9}$ $(HO+O_3)/k_{v=9}$ $(HO+H_2)$ required was at least a factor of 20 greater than obtained by Streit and Johnston.[3]

None of the systems used in these studies are sufficiently free of complications to be confident of the results from any one of them.

It seems that our previously recommended value for $k_{v=9}$ may be too low and, if this is so, it costs some doubt on the recommended values of k for $v<9$. We therefore make no recommendation. Further experimental studies are required.

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

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

$\Delta H^\circ(1) = \Delta H^\circ(2) = -166$ 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			
$(1.65\pm0.3)\times10^{-12}$(2.1–24.9 Torr He)	298	Rozenshtein *et al.*, 1984[1]	(a)
$k_1 = (1.5\pm0.4)\times10^{-12}$	298	Sander, 1984[2]	(b)
$k_1 = (1.6\pm0.1)\times10^{-12}$(2.4 Torr N_2, O_2)	295	Cattell *et al.*, 1986[3]	(c)
$k_1 = 1.88\times10^{-12}$	298	Kurylo, Oullette and Laufer, 1986[4]	(d)
$k_2 = 4.53\times10^{-32}[O_2]$			
$k_2 = 5.95\times10^{-32}[N_2]$			
$k_1 = (2.0\pm0.6)\times10^{-13}\exp[(595\pm120)T]$	253–390	Takacs and Howard, 1986[5]	(e)
$k_1 = (1.54\pm0.07)\times10^{-12}$	294		
$(2.7\pm0.6)\times10-{}^{12}$(760 Torr N_2)	299	Andersson, Cox and Jenkins, 1988[6]	(f)
$(4.1\pm1.0)\times10^{-12}$(760 Torr N_2)	278		
Branching Ratios			
$k_2/k_1 < 0.0022$	298	Glinski and Birks, 1985[7]	(g)
Reviews and Evaluations			
$k_1 = 2.2\times10^{-13}\exp(600/T)$	230–420	CODATA, 1984[8]	(h)
$k_2 = 1.9\times10^{-33}[N_2]\exp(980/T)$	230–420		
$k_1 = 2.3\times10^{-13}\exp(590/T)$	200–300	NASA, 1985[9]	(i)
$k_2 = 1.7\times10^{-33}[M]\exp(1000/T)$	200–300		
$k_1 = 2.3\times10^{-13}\exp(590/T)$	200–300	NASA, 1987[10]	(j)
$k_2 = 1.7\times10^{-33}[M]\exp(1000/T)$			

Comments

(a) Discharge flow study, He carrier gas. HO_2 produced by $F + H_2O_2$ and by $H + O_2 + M$. [H] and [F] measured by ESR. $[HO_2]$ monitored by LMR. Pressure varied over range 2.1–24.9 Torr He. Range of k values $(1.2–2.1)\times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} with no correlation with pressure.

(b) Discharge-flow study, He carrier gas. HO_2 produced by $F + H_2O_2$. $[HO_2]$ monitored by mass spectrometry. Absolute value of $[HO_2]$ based on UV absorption at 220 nm using σ values of Cox and Burrows.[11]

(c) Modulated photolysis of $Cl_2/CH_3OH/O_2$ mixtures. HO_2 monitored by infrared absorption at 1117 cm^{-1} using a tunable diode laser. Rise and decay of $[HO_2]$ gave k_1 an effective absorption cross section.

(d) Flash photolysis study. HO_2 generated using $Cl_2/CH_3OH/O_2$ mixtures and, in some case, $Cl_2/H_2/O_2$ mixtures. $[HO_2]$ monitored by UV absorption in multipass optical cell. NASA recommended values of σ used.[9] N_2 and O_2 mixtures used over total pressure range 25–760 Torr.

(e) Discharge flow study, He carrier gas. HO_2 produced by $F + H_2O_2$ and from $Cl_2/CH_3OH/O_2$ mixtures. $[HO_2]$ monitored by LMR.

(f) Molecular modulation study. HO_2 produced in flowing gas mixtures $(Cl_2/CH_3OH/N_2/O_2)$ by UV photolysis. $[HO_2]$ monitored by absorption at 220 nm using σ of Cox and Burrows.[11] Total k given by $9.2\times 10^{-15}\exp(1700/T) + 2.1\times 10^{-34}\exp(3000/T)\,[CH_3OH]$ cm^3 $molecule^{-1}$ s^{-1} in N_2 at 1 atm. based on measurements at 278 and 299 K only.

(g) Photolysis of $H_2O_2/H_2O/N_2$ mixtures at 253.7 nm and 298 K. Total pressue ~50 Torr, N_2 in excess. H_2 yield measured by gas chromatography.

(h) Accept values obtained by Kircher and Sander.[12]

(i) Expression for k_1 based on results of Cox and Burrows.[11] Kircher and Sander.[12] Thrush and Tyndall,[13,14] and Takacs and Howard.[15]

Expression for k_2 based on work of Sander *et al*,[16] Simonaitis and Heicklen,[17] and Kircher and Sander.[12]

(j) Based on references cited in (h) plus Kurylo *et al.*[4]

Preferred Values

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

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

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

$k_1 = 2.2\times 10^{-13}\exp(600/T)$ cm^3 $molecule^{-1}$ s^{-1} over range 230–429 K.

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

In the presence of H_2O the expressions for k_1 and k_2 should be multiplied by the term $(1 + 1.4\times 10^{-3}\exp[2200/T][H_2O])$.

Reliability

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

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

Comments on Preferred Values

All of the recent measurements are in excellent agreement with the previous CODATA recommendations.

Although the measurements of k at low pressures by Rozenshtein *et al.*[1] are in agreement with other studies under these conditions, in surveying all of the data available at that time Rozenshtein *et al.* conclude that there is no evidence that k varies with pressure. However, the contrary conclusion, favoring pressure effects and the occurrence of channel (2), has been strengthened by the recent work of Kurylo *et al.*[4] whose results for the effects on k of additions of N_2 and O_2 confirm quantitatively the earlier findings of Kircher and Sander[12] and of Simonaitis and Heicklen.[17]

There have been no recent experimental studies to check the marked effect of H_2O on the rate coefficient, but the recent work of Anderson *et al.*[6] shows that CH_3OH has a similar effect suggesting that it is typical of strong dipolar hydrogen bonding species. Mozurkewich and Benson[18] have considered the effect theoretically and conclude that the negative temperature dependence, the pressure dependence, and the observed isotope effects, can most reasonably be explained in terms of a cyclic hydrogen bonded, H_2OHO_2, intermediate in contrast to alternative structures suggested by others.

Sahetchain *et al.*[19] reported the formation of H_2 (~10% at 500 K) in the system but this is contrary to earlier evidence of Baldwin *et al.*[20] and the recent study of Glinski and Birks[6] who find $k_2/k_1 < 0.0022$ at 298 K.

Keyser *et al.*[21] have measured a yield of $O_2(b\,^1\Sigma_g^+)$ of $< 3\times 10^{-2}$ per HO_2 consumed.

The recommended expressions are unchanged from CODATA 1984.

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$HO_2 + O_3 \rightarrow HO + 2O_2$

$\Delta H^\circ = -118$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.9 \pm 0.3) \times 10^{-15}$	298	Manzanares *et al.*, 1986[1]	(a)
$(3.2 \pm 5.8) \times 10^{-13} \exp[-(1730 \pm 740)/T] + (1.2 \pm 0.5) \times 10^{-15}$	243–413	Sinha, Lovejoy, and Howard, 1987[2]	(b)
$(2.14 \pm 0.14) \times 10^{-15}$	297		
$(1.8 \pm 0.6) \times 10^{-14} \exp[-(680 \pm 148)/T]$	253–400	Wang, Suto, and Lee, 1988[3]	(c)
$(1.3 \pm 0.3) \times 10^{-15}$	233–253		
$(1.9 \pm 0.3) \times 10^{-15}$	298		
Reviews and Evaluations			
$1.4 \times 10^{-14} \exp(-600/T)$	250–400	CODATA, 1984[4]	(d)
$1.4 \times 10^{-14} \exp(-580/T)$	200–300	NASA, 1985[5]	(e)
$1.1 \times 10^{-14} \exp(-500/T)$	240–300	NASA, 1987[6]	(f)

Comments

(a) Discharge-flow study, He carrier gas. HO_2 produced by reaction sequence $Cl + CH_3OH \rightarrow CH_2OH + HCl$, $CH_2OH + O_2 \rightarrow HO_2 + CH_2O$. Excess of O_3 used. $[O_3]$ determined by absorptin at 253.7 nm. $[HO_2]$ monitored by photodissociation at 147 nm and detection of HO(A–X) fluorescence at 310 nm. C_2F_3Cl and C_3H_8 used as scavenger for HO produced from reaction.

(b) Discharge-flow study, He carrier gas. HO_2 radicals generated by reaction sequence $Cl + CH_3OH \rightarrow CH_2OH + HCl$, $CH_2OH + O_2 \rightarrow HO_2 + CH_2O$. ^{16}O and ^{18}O labeled species used $[H^{16}O]$, $[H^{18}O]$, $[H^{16}O_2]$, $[H^{18}O_2]$ monitored by laser magnetic resonance.

(c) Techniques as in (a) but only C_3H_8 used as HO scavenger.

(d) Accepts value at 298 K of Zahniser and Howard.[7]

(e) Accepts expression of Zahniser and Howard.[7]

(f) Based on work of Zahniser and Howard,[7] Manzanares *eta l.*[1] and Sinha *et al.*[2]

Preferred Values

$k = 2.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.4 \times 10^{-14} \exp(-600/T)$ cm^3 molecule^{-1} s^{-1} over range 250–300 K.

Reliability

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

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

Comments on Preferred Values

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

For modeling at temperatures is the range 200–250 K at value of $k = 1.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} should be used.

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[6] NASA Evaluation No. 8, 1987 (See References in Introduction).

$H_2O_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°/kJ mol^{-1}	λ threshold/nm
$H_2O_2 + h\nu \rightarrow HO + HO$	(1)	207	578
$\rightarrow H_2O + O(^1D)$	(2)	328	365
$\rightarrow H + HO_2$	(3)	360	332
$\rightarrow HO + HO(^2\Sigma)$	(4)	598	200

Absorption cross section data

Wavelength range/nm	References	Comment
190–350	Molina and Molina, 1981[1]	(a)
193–350	Nicovich and Wine, 1988[2]	(b)

Comments

(a) Measured at 298 K with spectral resolution of 0.3–0.5 nm. These results supersede the earlier results of Molina, Schinke, and Molina,[3] which were slightly higher.

(b) Relative cross sections measured over the temperature range 300–380 K at 285 K for the wavelength range 230–295 nm. Room temperature literature values at 202.6 and at 228.8 nm were used for absolute calibration. A significant temperature dependence was observed for the wavelength range 310–350 nm, and a simple model was used to extrapolate results to lower temperatures. Upper tropospheric photodissociation rates were calculated.

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
190	67.2	275	2.5
195	56.3	280	2.0
200	47.5	285	1.5
205	39.8	290	1.13
210	34.9	295	0.87
215	29.9	300	0.66
220	25.4	305	0.49
225	21.3	310	0.37
230	17.9	315	0.28
235	14.8	320	0.20
240	12.2	325	0.16
245	10.0	330	0.12
250	8.3	335	0.09
255	6.7	340	0.07
260	5.2	345	0.05
265	4.2	350	0.03
270	3.2		

Quantum yields

$\phi_1 = 1.0$ throughout this wavelength range.

Comments on Preferred Values

The preferred absorption cross section values have been derived by averaging the results of Molina and Molina[1] and the earlier results of Lin, Rohatgi, and DeMore,[4] which are in good agreement. These recommended values are slightly small than those given in the previous evaluation of data for this process.[5] The recommended quantum yield values are unchanged from the evaluation, where the reader can also find absorption cross section values at 600 and 1100 K.

There have been a number of studies of the product HO state distribution from the laser photodissociation of H_2O_2 at 193, 248, and 266 nm.[6–13] The results at all three wavelengths are similar. They show that almost all of the total excess energy appears as translational energy of recoil of the HO fragments, with the remainder (10–15%) going into rotational excitation of the HO. Vibrational excitation was not observed. A quantum yield of 0.12 ± 0.10 for hydrogen atom production was reported in one study of H_2O_2 photodissociation at 193 nm.[14]

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4.3. Nitrogen Species

$O + NO_2 \rightarrow O_2 + NO$

$\Delta H = -192$ kJ mol^{-1}

Rate coefficient data

$k/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.00 \pm 0.10) \times 10^{-11}$	298	Ongstad and Birks, 1984[1]	(a)
$(6.58 \pm 0.52) \times 10^{-12} \exp[(142 \pm 23)/T]$	224–354	Ongstad and Birks, 1986[2]	(a)
$(1.03 \pm 0.09) \times 10^{-11}$	298		
$(5.21 \pm 0.50) \times 10^{-12} \exp[(202 \pm 27)/T]$	233–357	Geers-Muller and Stuhl, 1987[3]	(b)
$(1.02 \pm 0.02) \times 10^{-11}$	301		
Reviews and Evaluations			
9.3×10^{-12}	230–340	CODATA, 1984[4]	(c)
9.3×10^{-12}	200–300	NASA, 1985[5]	(c)
$6.5 \times 10^{-12} \exp(120/T)$	200–300	NASA, 1987[6]	(d)

Comments

(a) Discharge flow system at 2.3 Torr total pressure. Decay of oxygen atoms in excess NO_2 monitored by chemiluminescent reaction with NO.

(b) H_2-laser photolysis system at 6.0 Torr total pressure. Oxygen atoms generated by NO photolysis and their decay in excess NO_2 monitored by chemiluminescent reaction with NO. Values of rate coefficients for reactions of oxygen atoms with N_2O_4 and N_2O_5 at 199 K were estimated.

(c) Based on data of Davis *et al.*,[7] Bemand *et al.*,[8] and Slanger *et al.*[9]

(d) Based on data of David *et al.*,[7] Bemand *et al.*,[8] Slanger *et al.*,[9] Ongstad and Birks,[2] and Geers-Muller and Stull.[3]

Preferred Values

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

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

Reliability

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

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

Comments on Preferred Values

The preferred value at 298 K is the average of the values reported by Ongstad and Birks,[1] Geers-Muller and Stuhl,[2] Davis *et al.*,[7] Bemand *et al.*,[8] and Slanger *et al.*[9] The recommended temperature dependence results from a least-squares fit to the data of Ongstad and Birks,[2] Geers-Muller and Stuhl,[3] and Davis *et al.*,[7] and the preexponential factor has been adjusted to fit the preferred value of k (298 K).

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$N + O_2 \rightarrow NO + O$

Comment

Since the previous evaluation of the data for this reaction (Ref. 1), there have been two studies of this system. Winkler *et al.*[2] determined the vibrational state distribution ($v = 0$–7) of the product NO using two-photon ionization spectroscopy. Barnett, Marston, and Wayne[3] using a discharge flow-chemiluminescence technique determined a room temperature rate coefficient in excellent agreement with the recommendation in Ref. 1, which is left unchanged.

References

[1] CODATA, 1980 (See references in Introduction)
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$N + O_3 \rightarrow NO + O_2$

$\Delta H = -525$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.0 \pm 0.2) \times 10^{-16}$	298	Barnett, Marston, and Wayne, 1987[1]	(a)
$< 1 \times 10^{-15}$	298	CODATA, 1984[2]	(b)
$< 1 \times 10^{-15}$	298	NASA, 1985[3]	(b)
$< 1 \times 10^{-15}$	298	NASA, 1987[4]	(b)

Comments

(a) Discharge flow-chemiluminescence technique. First-order decay of N atoms in excess O_3 monitored by emission from the first positive band system of N_2 resulting from recombination of N atoms. Higher effective values of k observed at low ozone concentrations. For $[O_3] > 5 \times 10^{15}$ molecule cm^{-3}, the effective value of k is independent of ozone concentration.

(b) Upper limit based on results of Stief *et al.*[5] in flash photolysis and discharge flow systems with N atoms monitored by resonance fluorescence. No decay was observed, limit based on detection sensitivity.

Preferred Values

$k = 1.0 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value accepts the very recent results of Barnett *et al.*[1] In this study the rate coefficient was measured under conditions which minimized the effects of impurities formed in the discharge. The value reported is consistent with the upper limit recommended in the previous evaluation[2] which was based on the results reported by Stief *et al.*[5]

References

[1] A. J. Barnett, G. Marston, and R. P. Wayne, J. Chem. Soc. Faraday Trans 2 **83**, 1453 (1987).

[2] CODATA Supplement II, 1984 (See references in Introduction).

[3] NASA Evaluation No. 7, 1985 (See references in Introduction).

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[5] L. J. Stief, W. A. Payne, J. H. Lee, and J. V. Michael, J. Chem. Phys. **70**, 5241 (1979).

$HO + NH_3 \rightarrow H_2O + NH_2$

$\Delta H^\circ = -50$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.55 \pm 1.1) \times 10^{-12} \exp[-(973 \pm 78)/T]$	297–364	Stephens, 1984[1]	(a)
$(1.73 \pm 0.11) \times 10^{-13}$	297		
see note	840–1425	Jeffries and Smith, 1986[2]	(b)
Reviews and Evaluations			
$3.3 \times 10^{-12} \exp(-900/T)$	230–450	CODATA, 1984[3]	(c)
$3.5 \times 10^{-12} \exp(-925/T)$	230–450	NASA, 1985[4]	(d)
$3.6 \times 10^{-12} \exp(-930/T)$	230–450	NASA, 1987[5]	(e)

Comments

(a) Discharge flow-resonance fluorescence technique. Total pressure was 1 Torr He. Rate constant for quenching of $HO(A\,^2\Sigma^+)$ by NH_3 was determined to be 9.6×10^{-10} cm^3 molecule^{-1} s^{-1}.

(b) Infrared laser pyrolysis technique with LIP detection of HO. Data confirm curvature in Arrhenius plot which had been inferred from comparison of earlier work at high and low temperatures. Authors combine their data with data from ten other studies to derive expression: $k = 1.58 \times 10^{-17} T^{1.8} \exp(-250/T)$ cm^3 molecule^{-1} s^{-1} for the temperature range 225–2350 K.

(c) Based on data of Stuhl,[8] Smith and Zellner,[7] Perry *et al.*,[8] and Silver and Kolb.[9]

(d) Based on data cited in comment (c) and data of Stephens.[1]

(e) Based on data cited in (d) with rounded value of E/R.

Preferred Values

$k = 1.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

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

Reliability

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

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

Comments on Preferred Values

The preferred value at room temperature is based on the results of Stuhl,[6] Smith and Zellner,[7] Perry *et al.*,[8] Silver and Kolb,[9] and Stephens.[1] The temperature dependence is based on results reported by Smith and Zellner,[7] Perry *et al.*,[8] Silver and Kolb,[9] and Stephens.[1] There is only a minor change from the previous CODATA recommendation,[3] resulting from inclusion of the new data by Stephens.[1] The many high temperature studies have been considered by Jeffries and Smith[2] to derive a modified Arrhenius expression over an extended temperature range [see comment (b)].

References

[1] R. D. Stephens, J. Phys. Chem. **88**, 3308 (1984).

[2] J. B. Jeffries and G. P. Smith, J. Phys. Chem. **90**, 487 (1986).

[3] CODATA Supplement II, 1984 (See references in Introduction).

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$HO + HONO \rightarrow NO_2 + H_2O$

$\Delta H = -168$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.80 \pm 0.36) \times 10^{-11} \exp(-(390 \pm 80)/T)$	278–342	Jenkin and Cox,1987[1]	(a)
4.50×10^{-12}	295		
Relative Rate Coefficient			
$(6.3 \pm 0.3) \times 10^{-12}$	296	Cox, Derwent, and Holt[2]	(b)

Comments

(a) Modulated photolysis of O_3 at 254 nm in presence of H_2O and HONO in Ar at 11 Torr. Time-resolved behavior of OH radicals intermittently generated in presence of excess HONO was monitored by resonance absorption at 308 nm.

(b) Photolysis of HONO in presence of added H_2, CH_4, CO_2, CO, and NO at room temperature and atmospheric pressure. Measured ratio $k/k(HO + H_2) = 945 \pm 48$. Value of k given here calculated using $k(HO + H_2) = 6.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (IUPAC value).

Preferred Values

$k = 4.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.8 \times 10^{-11} \exp(-390/T)$ cm^3 molecule^{-1} s^{-1} over range 280–340 K.

Reliability

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

$\Delta(E/R) = \pm 400$ K

Comments on Preferred Values

The preferred value is based on the recent results of Jenkin and Cox.[1] This is the only direct determination of this rate coefficient. The agreement between these results at low pressure and the earlier, indirect results of Cox *et al.*[2] at atmospheric pressure suggests that any pressure dependence of this rate is small.

Reference

[1] M. E. Jenkin and R. A. Cox, Chem. Phys. Lett. **137**, 548 (1987).
[2] R. A. Cox, R. G. Derwent, and P. M. Holt, J. Chem. Soc. Faraday Trans. 1 72, 2031 (1976).

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

$\Delta H^\circ = -75$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.4 \times 10^{-15} \exp(843/T)$	253–295	Devolder *et al.*, 1984[1]	(a)
$(0.93 \pm 0.10) \times 10^{-13}$	295		
$(1.26 \pm 0.11) \times 10^{-13}$	298	Jolly, Paraskevopoulos, and Singleton, 1985[2]	(b)
$(2.16 \pm 0.15) \times 10^{-13}$ 10 Torr N_2	248	Stachnik, Molina, and Molina, 1986[3]	(c)
$(1.28 \pm 0.10) \times 10^{-13}$ 10 Torr N_2	297		
Reviews and Evaluations			
$9.4 \times 10^{-15} \exp(778/T)$	220–300	CODATA, 1984[4]	(d)
see note	220–300	NASA, 1985[5]	(e)
see note	220–300	NASA, 1987[8]	(e)

Comments

(a) Discharge flow-resonance fluorescence system. Arrhenius expression quoted applies to results below room temperature. Rate coefficient was measured up to 373 K and found to level off above room temperature.

(b) Laser flash photolysis-resonance absorption technique. HNO_3 photolyzed at 222 nm. Value given is for pressures of 1–16 Torr HNO_3. Experiments also done in presence of 500 Torr N_2 and 600 Torr SF_6. After corrections for contribution of reaction $OH + NO_2 + M$ were made, no significant effect of total pressure on k was observed.

(c) Laser flash photolysis-resonance absorption technique. HNO_3 photolyzed at 193 nm. Measurements made at 10, 60, and 730 Torr of He, N_2, and SF_6. NO_2 was determined to be less than 0.1%. Data were fit to fall off function given in Lamb *et al.*[14] Extrapolated zero-pressure rate constants correspond to $E/R = -710$ K.

(d) Based on data of Wine *et al.*,[7] Margitan and Watson,[8] Kurylo *et al.*,[9] Jourdian *et al.*,[10] Marinelli and Johnston,[11] Smith *et al.*,[12] and Ravishankara *et al.*[13]

(e) Based on data cited in (d) and date in Ref. 1–3. Data were fit to fall off expression given in Lamb *et al.*[14]

Preferred Values

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

See comments for expression to be used under other conditions of T and P. *Reliability*

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

Comments on Preferred Values

There have been many studies of this reaction recently which have significantly improved our understanding of the kinetics and mechanism. From these studies there is general consensus on the following major features of the data: a strong negative temperature dependence below room temperature with a much weaker temperature dependence above room temperature which appears to level off near 500 K, and (b) a small but measurable pressure dependence at room temperature which increases at low temperatures. The pressure dependence from 20–100 Torr and 225–298 K was determined by Margitan and Watson,[8] and Stachnik *et al.*[3] measured the rate precisely over the range 10–730 Torr at 297 K and 248 K. These studies agree on a 50% increase in the rate constant at the highest pressure studied at room temperature and a doubling of the low-pressure value at 240 K. Lamb *et al.*[14] have proposed a mechanism involving formation of a bound, relatively long-lived, intermediate complex. This mechanism gives a rate coefficient expression which combines a low pressure limiting rate constant (k_1) and a Lindemann–Hinshelwood expression for the pressure dependence. This mechanism has been used in the NASA evaluation,[6] and the expression derived in the NASA panel's analysis has been adopted for the evaluation. The overall rate constant can be expressed as.: $k = k_1\ (T) + k_2\ (\mathrm{M},T)$ where $k_2\ (\mathrm{M},T) = k_3[M]/(1 + k_3[\mathrm{M}]/k_4)$. The expressions for the elementary rate constants are: $k_1 = 7.2\times10^{-15}\ \exp(785/T)$ cm^3 molecule^{-1} s^{-1}, $k_3 = 1.9\times10^{-33}\ \exp(725/T)$ cm^6 molecule^{-2} s^{-1}, and $k_4 = 4.1\times10^{-16}\exp(1440/T)$ cm^3 molecule^{-1} s^{-1}; all expressions are valid over the temperature range 220–300 K. This expression has been evaluated for the conditions of 298 K and 1 atm pressure to yield the preferred value given here. The reader is referred to Ref. 6 for a more detailed discussion of this reaction. Bossard *et al.*[15] have reported a significant pressure dependence of the rate constant for the related reaction OD + DNO_3.

References

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

[2] G. S. Jolly, G. Paraskevopoulos, and D. L. Singleton, Chem. Phys. Lett. **117**, 132 (1985).

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

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[5] NASA Evaluation No. 7, 1985 (See references in Introducton).

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[7] P. H. Wine, A. R. Ravishankara, N. M. Kreutter, R. C. Shah, J. M. Nicovich, R. L. Thompson, and D. J. Wuebbles, J. Geophys. Res. **86**, 1105 (1981).

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[14] J. J. Lamb, M. Mozurkewich, and S. W. Benson, J. Phys. Chem. **88**, 6441 (1984).

[15] A. R. Bossard, G. Paraskevopoulos, and D. L. Singleton, Chem. Phys. Lett. **134**, 583 (1987).

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

$\Delta H^\circ\ (1) = -194$ kJ mol^{-1}
$\Delta H^\circ\ (2) = -50$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(5.5 \pm 1.4)\times10^{-12}$	268–295	Barnes *et al.*, 1986[1]	(a)
Reviews and Evaluations			
$1.3\times10^{-12}\exp(380/T)$	240–340	CODATA, 1984[2]	(b)
$1.3\times10^{-12}\exp(380/T)$	240–340	NASA, 1985[3]	(b)
$1.3\times10^{-12}\exp(380/T)$	240–340	NASA, 1987[4]	(c)

Comments

(a) Relative study over pressure range 1–300 Torr ($\mathrm{M} = \mathrm{He},\mathrm{N}_2$) in a 420 L static reaction vessel. HO_2NO_2 monitored by FTIR spectroscopy; reference hydrocarbons-(propene, butane) monitored by gas chromatography. k(OH + propene) values as factor of T and P taken from Klein *et al.*[5] and Zellner and Lorenz[6]. k(OH + butane) taken as 2.5×10^{-12} cm^3 molecule^{-1} s^{-1} with an activation energy of 4.6 kJ mol^{-1}. Rate coefficient reported to be independent of T and P over ranges studied.

(b) Based on data of Trevor *et al.*,[7] Smith *et al.*,[8] and Barnes *et al.*[9]

(c) Based on data of Trevor *et al.*,[7] Smith *et al.*,[8] Barnes *et al.*[9] and Barnes *et al.*[1]

Preferred Values

$k = 5.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

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

Reliability

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

$\Delta(E/R) = {}^{+300}_{-600}$ K.

Comments on Preferred Values

The preferred value is based on a least-squares fit to the data of Trevor *et al.*,[7] Smith *et al.*,[8] and Barnes *et al.*[1] Trevor *et al.*[7] studied this reaction from 246–324 K at low pressure (3–15 Torr) and recommended a temperature independent value, but also reported an Arrhenius expression with $E/R = (193 \pm 194)$K. In contrast Smith *et al.*[8] report data from 240–340 K at 1 atom pressure and report a negative temperature dependence with $E/R = -(650 \pm 30)$K. It is possible that the difference may be due to the reaction being complex with different temperature dependences at low and at high pressure. The error limits on the recommended E/R value encompass the results of both studies. At 220 K the values deduced from these studies differ by a factor of 3. The recent study of Barnes *et al.*,[1] the first study over an extended pressure range, found the rate coefficient to be independent of pressure from 5 to 300 Torr at 278 K and also report the same value at 295 K (low pressure) and at 268 K (100 Torr He). They also report no change with synthetic air as buffer gas. A TST calculation by Lamb *et al.*[10] suggests that the pressure dependence for this rate coefficient will be much less than that for the corresponding reaction of HO with HNO_3.

References

[1] I. Barnes, V. Bastian, K. H. Becker, E. H. Fink, and F. Zabel, Chem. Phys. Lett. **123**, 28 (1986).

[2] CODATA Supplement II, 1984 (see references in Introduction).

[3] NASA Evaluation No. 7, 1985 (see references in Introduction).

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[9] I. Barnes, V. Bastian, K. H. Becker, E. H. Fink, and F. Zabel, Chem. Phys. Lett. **83**, 459 (1981).

[10] J. J. Lamb, M. Mozurkewich, and S. W. Benson, J. Phys. Chem. **88**, 6441 (1984).

$HO + NO_2 + M \rightarrow HONO_2 + M$

$\Delta H^\circ = -207.6$ kJ mol^{-1}

Comment

Burkholder, Hammer, and Howard[1] by combination of a high-resolution Fourier transform spectrometer to a fast flow multipass absorption cell have studied the structure of the product of the reaction. HOONO was not detected. A 75% (+25%, −10%) conversion of HO to $HONO_2$ was measured. The observations are rationalized in terms of unimolecular rate theory. The discrepancies between the CODATA recommendations[2] of k_0 and k_∞ and the corresponding NASA recommendations[3] are due to the use of different F_c values, i.e., a standard value of $F_c = 0.6$ was employed in Ref. 3, whereas individual F_c values were used in Ref. 2 such as F_c (300 K) = 0.43. The experimental data are reproduced equally well by the two representations.

References

[1] J. B. Burkholder, P. O. Hammer, and C. J. Howard, J. Phys. Chem. **91**, 2136 (1987).

[2] COOATA Supplement II, 1984 (see references in Introduction).

[3] NASA Evaluation No. 8, 1987 (see references in Introduction).

$HO + NO_3 \rightarrow HO_2 + NO_2$

$\Delta H^\circ = -64.3$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.6 \pm 0.6) \times 10^{-11}$	298	Mellouki, Le Bras and Poulet, 1988[1]	(a)
$(2.0 \pm 0.6) \times 10^{-11}$	298	Boodaghians *et al.*, 1988[2]	(b)

Comments

(a) Discharge flow—EPR monitoring of HO and HO_2 (after conversion to HO) in the presence of excess NO_3, which was measured by titration with NO or 2,3 dimethyl-2-butene. Complex kinetic behavior to extract k values.

(b) Discharge flow—resonance fluorescence detection of OH. NO_3 by long path absorption at 662 nm. H + NO_2 reaction used to generate OH and F + HNO_3 to produce NO_3, which was in excess over OH. k value corrected for secondary reactions which accelerates OH decay.

Preferred Values

$k = 2.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$.

Comments on Preferred Values

The two measurements of this rate constant using the discharge flow technique are in good agreement, although in both systems corrections for secondary reactions were required. In the absence of experimental data a temperature dependence cannot be recommended. In line with other radical + radical reactions a small negative temperature coefficient is expected.

References

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

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

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

$\Delta H^\circ = -105$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.5×10^{-31} [N_2]	298	Kurylo and Ouelette 1986[1]	(a)
1.3×10^{-31} [O_2]	298		
$1.8\times10^{-31}(T/300)^{-3.2\pm0.4}$ [N_2]	228–358	Kurylo and Ouelette 1986[2]	(a)
Reviews and Evaluations			
$2.3\times10^{-31}(T/300)^{-4.6}$ [N_2]	200–300	CODATA, 1984[3]	(b)
$2.1\times10^{-31}(T/300)^{-4.6}$ [O_2]	200–300		
$1.8\times10^{-31}(T/300)^{-3.2}$ [air]	200–300	NASA, 1987[4]	(c)

Comments

(a) Flash photolysis of Cl_2–CH_3OH-NO_2 mixtures in presence of O_2 or N_2. HO_2 detection at 225 nm. Falloff curve measured over the pressure range 25–600 Torr. Evaluation of the new data together with those by Sander and Peterson[5] using $F_c = 0.6$ and $k_\infty = 4.7\times10^{-12}(T/300)^{-1.4\pm1.0}$ cm^3 molecule^{-1} s^{-1}.

(b) Based on data by Sander and Peterson[5] in excellent agreement with earlier results.

(c) Based on the analysis from Ref. 2 of the data from Refs. 1, 2, and 5.

Preferred Values

$k_0 = 1.8\times10^{-31}(T/300)^{-3.2}$ [N_2] cm^3 molecule^{-1} s^{-1} over the range 220–360 K.

$k_0 = 1.5\times10^{-31}(T/300)^{-3.2}$ [O_2] cm^3 molecule^{-1} s^{-1} over the range 220–360 K.

Reliability

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

$\Delta n = +1$.

Comments of Preferred Values

The new data are in excellent agreement with the older results. The analysis of the combined data from Refs. 1, 2, and 5 shows a very consistent picture.

High-pressure rate coefficient
Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
5.5×10^{-12}	298	Kurylo and Ouelette, 1986[1]	(a)
$4.7\times10^{-12}(T/300)^{-1.4\pm1.0}$	228–358	Kurylo and Ouelette, 1987[2]	(a)
Reviews and Evaluations			
$4.2\times10^{-12}(T/300)^{0.2}$	200–300	CODATA, 1984[3]	(b)
$4.7\times10^{-12}(T/300)^{-1.4}$	200–300	NASA, 1987[4]	(c)

Comments

(a)–(c) See comments for k_0.

Preferred Value

$k_\infty = 4.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.1$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Value

The recommended values are from the analysis of the combined data from Refs. 1, 2, and 5. The available data provide a very consistent picture. A more accurate determination of the temperature coefficient of k_∞ would require measurements at pressures above 1 atm. Before these are available we prefer a temperature independent k_∞ value in agreement with other reactions (see also discussion of intermediate falloff range).

Intermediate Falloff Range

The given falloff expressions have been evaluated with a fixed value of $F_c = 0.6$. Neglecting the temperature dependence of F_c may result in too large negative T-exponents of k_∞.

References

[1] M. J. Kurylo and P. A. Ouelette, J. Phys. Chem. **90**, 441 (1986).
[2] M. J. Kurylo and P. A. Ouelette, J. Phys. Chem. **91**, 3365 (1987).
[3] COOATA Supplement II, 1984 (See references in Introduction).
[4] NASA Evaluation NO. 8, 1987 (See references in Introduction).
[5] S. P. Sander and M. E. Peterson, J. Phys. Chem. **88**, 1566 (1984).

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

$\Delta H(1) = -222.5$ kJ mol^{-1}
$\Delta H^\circ(2) = -14.9$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_1 = (9.24 \pm 4.8) \times 10^{-13}$	298	Mellouki, Le Bras, and Poulet, 1988[1]	(a)
$k_2 = (3.6 \pm 0.9) \times 10^{-12}$			
$(2.7^{+2.8}_{-1.8}) \times 10^{-12} \exp[(170 \pm 270)/T]$	263–338	Hall *et al.*, 1988[2]	(b)
4.06×10^{-12}	298		
$k_2/k < 0.6$			

Comments

(a) Discharge flow—EPR monitoring of OH and HO_2 (after conversion to HO) in the presence of excess NO_3, which was measured by titration with NO or 2,3 dimethyl 2 butene. Complex kinetic behavior of OH and HO_2 modeled to extract $k(HO_2 + NO_3)$ and $k(OH + O_3)$ for which a value of $(2.6 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was obtained.

(b) Molecular Modulation—UV (for HO_2) and Visible (for NO_3) absorption spectroscopy. Using photolysis of CL_2 in the presence of $ClONO_2$, H_2, and O_2 to produce the radicals. Rate coefficients obtained by computer fitting of complex kinetics. The upper limit of k_2/k was obtained from measurement of HO by modulated resonance absorption.

Preferred Values

$k = 4.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The two recent direct studies the only kinetic information on this reaction. The values obtained for the overall rate coefficient are in good agreement; despite the need in both cases to analyze complex kinetics to extract the k values. There is a discrepancy in the reported values for the branching ratio although Hall *et al.*[2] accept that their measurements are not definitive. The preferred value at 298 K is a mean from the two studies. No recommendation is made for the branching ratio or the temperature dependence because of the experimental uncertainties. For stratospheric modeling a temperature independent rate with branching ratios given by Mellouki *et al.*[1] is probably the best available choice.

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$NH_2 + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$< 1.5 \times 10^{-36}$ [N_2]	295	Patrick and Golden, 1984[1]	(a)
$< 3 \times 10^{-18}$	298	Lozovsky, Ioffe, and Sarkisov, 1984[2]	(b)
$< 7.7 \times 10^{-18}$	298	Michael *et al.*, 1985[3]	(c)
Reviews and Evaluations			
$< 3 \times 10^{-18}$	298	CODATA, 1984[4]	(d)
$< 3 \times 10^{-18}$	298	NASA, 1985[5]	(e)
$< 3 \times 10^{-18}$	298	NASA, 1987[6]	(f)

Comments

(a) Laser flash photolysis of O_3 at 248 nm in presence of NH_3. Decay of NH_2 monitored by laser resonance absorption spectroscopy at 598 nm. NH_2 decayed by reaction with O_3 and with NH_2. Up to 15 Torr O_2 added to system at total pressure of 230 Torr but no increase in decay rate was observed. Equivalent to bimolecular rate constant $< 1 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}.

(b) Flash photolysis of $NH_3/O_2/N_2$ mixtures at total pressures less than 30 Torr. $[NH_2]$ decay monitored by intracavity laser absorption spectroscopy at 598 nm. Decay rate observed to be independent of $P(O_2)$ above 1 Torr. Observed decay attributed to reaction $NH_2 + HO_2$.

(c) Flash photolysis—laser induced fluorescence study. NH_2 radicals produced by flash photolysis of NH_3 and observed in fluorescence at 578 nm after excitation by pumped dye laser. Total pressure of 25 Torr He. No increase in decay rate with increasing $[O_2]$ observed at low flash energy. Additional experiments done in presence of sufficient C_2H_4 to scavenge H atoms formed in NH_3 photolysis.

(d) Based on data of Lesclaux and Demissy[7] and Cheskis and Sarkisov.[8]

(e) Based on data of Lesclaux and Demissy,[7] Cheskis and Sarkisov,[8] Patrick and Golden,[1] and Lozovsky *et al.*[2]

(f) Based on data cited in (e) and data of Michael *et al.*[3]

Preferred Values

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

Comments on Preferred Values

The preferred value is based on the upper limits reported by Lesclaux and Demissy,[7] Cheskis and Sarkisov,[8] Patrick and Golden,[1] Lozovsky *et al.*,[2] and Michael *et al.*[3] In most systems HO_2 radicals were produced from the H atoms formed in the initial photolysis of NH_3, and NH_2 decay by reaction with HO_2 was observed. Patrick and Golden[1] produced NH_2 radicals in the absence of H atoms and observed no reaction with O_2. Hack *et al.*[9] produced NH_2 radicals in the absence of H atoms by the reaction of F atoms with NH_3 in a discharge flow reactor at low pressures and reported a third order reaction with O_2. However the weight of evidence from the other studies indicates that there is no observable reaction. It is possible that heterogeneous processes were important in their system. Hack and Kurzke[10] have studied the reaction NH_2 with electronically excited $O_2(^1\Delta)$ and reported a rate constant value of 1×10^{-14} cm^3 molecule^{-1} s^{-1} for this reaction.

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$NH_2 + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.57 \pm 0.5) \times 10^{-11} \exp(-(1151 \pm 123)/T)$	272–348	Patrick and Golden, 1984[1]	(a)
$(3.25 \pm 0.27) \times 10^{-13}$	298		
$(1.5 \pm 0.3) \times 10^{-13}$	298	Cheskis *et al.*, 1985[2]	(b)
Reviews and Evaluations			
$3.4 \times 10^{-12} \exp(-1000/T)$	250–380	CODATA, 1984[3]	(c)
$4.8 \times 10^{-12} \exp(-930/T)$	250–360	NASA, 1985[4]	(d)
$4.8 \times 10^{-12} \exp(-930/T)$	250–360	NASA, 1987[5]	(d)

Comments

(a) Laser flash photolysis of O_3 at 248 nm in presence of NH_3. Decay of NH_2 monitored by laser resonance absorption spectroscopy at 598 nm.

(b) Laser flash photolysis of O_3 at 266 nm in presence of NH_2. Decay of NH_2 monitored by laser induced fluorescence at 598 nm. Also measured rate coefficient for reaction of vibrationally excited NH_2 with O_3 and found it to be a factor of 10 faster.

(c) Based on data of Kurasawa and Lesclaux,[6] Bulatov *et al.*,[7] and Hack *et al.*[8]

(d) Based on data of Bulatov *et al.*,[7] Hack *et al.*,[8] and Patrick and Golden.[1]

Preferred Values

$k = 1.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.9 \times 10^{-12} \exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} over range 250–380 K.

Reliability

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

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

Comments on Preferred Values

The reported rate coefficients at room temperature vary by a factor of 5, ranging from 6×10^{-14} cm^3 molecule^{-1} s^{-1} in Ref. 6 to 3×10^{-13} in Ref. 1. There is no convincing argument for rejecting any of these results, and therefore the preferred value is taken as the average of the results reported by Kurasawa and Lesclaux,[8] Bulatov *et al.*,[7] Hack *et al.*,[8] Patrick and Golden,[1] and Cheskis *et al.*[2] The temperature dependence averages the values reported by Kurasaw and Lesclaux,[6] Hack *et al.*,[8] and Patrick and Golden.[1] Although the products of this reaction have not been determined, the most likely process is abstraction of an oxygen atom by NH_2 to give $NH_2O + O_2$. While it has been suggested[7,8] that NH_2 may be regenerated by reaction of NH_2O with O_3, recent work[1] indicates that this reaction must be slow.

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

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

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.81\pm0.12)\times10^{-11}$	297	Whyte and Phillips, 1983[1]	(a)
1.7×10^{-11}	298	Dreier and Wolfrum, 1985[2]	(b)
$(1.3\pm0.4)\times10^{-11}$	298		
Branching Ratios			
$(k_2+k_3)/k = 0.13\pm0.02$	298	Hall *et al.*, 1986[3]	(c)
$(k_2+k_3)/k < 0.13$	300	Dolson, 1986[4]	(d)
$(k_2+k_3)/k = 0.12$	298	Silver and Kolb, 1987[5]	(e)
See comments		Crowley and Sodeau, 1987[6]	(f)
Reviews and Evaluations			
$1.6\times10^{-11}(T/298)^{-1.5}$	210–500	CODATA, 1984[7]	(g)
$3.8\times10^{-12}\exp(450/T)$	200–300	NASA, 1985[8]	(h)
$3.8\times10^{-12}\exp(450/T)$	200–300	NASA, 1987[9]	(h)

Comments

(a) Laser flash photolysis NH_3 at 193 nm. NH_2 decay monitored by laser induced fluorescence at 598 nm. Total pressure of 1–2 Torr

(b) Flow reactor. Laser flash photolysis of NH_3 at 193 nm. NH_2 radicals and product N_2 monitored by CARS (coherent anti-stokes Raman spectroscopy). Independent value of rate coefficient obtained from time-resolved IR fluorescence of vibrationally excited H_2O. Vibrational population distributions in product H_2O and N_2 were determined.

(c) Infrared kinetic spectroscopy method using laser flash photolysis of NH_3 at 193 nm and color center laser probing of species from 2.3 to 3.2 μm. Yields of OH and H_2O were determined. Evidence for production of H_2O in very high vibrational states shown by pronounced delay in absorption lines originating from the ground vibrational state.

(d) Fast-flow tube reactor coupled to a modulated beam mass spectrometer. Hydroxyl radicals reacted with added CO to give CO_2 with scavenging efficiency near unity. $[HO]/H_2O]$ product ratio determined from ratio of CO_2^+ and H_2O^+ ion intensities.

(e) Reevaluation of branching ratio data reported in an earlier paper[10] by same authors, who now conclude that branching ratio is less than 0.33 having a most probable value of 0.12.

(f) Photolysis of NH_3 at 184.9 nm in presence of NO in argon, nitrogen, and neon matrices at 4.2 K in conjunction with FTIR spectroscopy of isotopically labeled species. Authors conclude that N_2O is a direct product of this reaction and that the formation of H_2O and N_2 is inefficient in a low temperature matrix.

(g) Based on data of Stief *et al.*,[11] Silver and Kolb,[10] Andresen *et al.*,[12] Gordon *et,al.*,[13] Gehring *et al.*,[14] Hancock *et al.*,[15] Sarkisov *et al.*,[18] Lesclaux *et al.*,[17] and Hack *et al.*[18]

(h) Based on data cited in (g) and data of Whyte and Phillips.[1]

Preferred Values

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

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

Reliability

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

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred value for k at 298 K is the average of the values reported by Whyte and Phillips,[1] Dreier and Wolfrum[2], Silver and Kolb,[10] Stief *et al.*,[11] Andresen *et al.*,[12] Gordon *et al.*,[13] Gehring *et al.*,[14] Hancock *et al.*,[15] Sarkisov *et al.*,[16] Lesclaux *et al.*,[17] and Hack *et al.*[18] The values reported in these studies range from $(8–27) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The flash photolysis results average 19×10^{-12} while the discharge-flow results average 9×10^{-12} cm^3 molecule^{-1} s^{-1}. This discrepancy cannot be accounted for simply on the basis of a pressure effect as the pressure ranges of the two types of studies overlapped and no single study observed a pressure dependence. The temperature dependence is based on the data below 500 K in the four temperature-dependent studies—Silver and Kolb,[10] Stief *et al.*,[11] Lesclaux *et al.*,[17] and Hack *et al.*[18] There now appears to be more or less general agreement that at room temperature reaction channel (1) to give $N_2 + H_2O$ dominates and that the direct production of HO is small. Silver and Kolb[5] reanalyzed their earlier data and now believe that most of the HO observed came from the reaction NH with NO. The new studies of Hall *et al.*[3] and Dolson[4] as well as the earlier study of Stief *et al.*[11] agree that channels (2) and (3) to give HO are much less important than channel (1) to give H_2O. However, Andresen *et al.*[12] reports that the production of HO predominates, and this discrepancy has not been explained. Reaction channel (1) is very exothermic and vibrationally excited H_2O has been observed by Gehring *et al.*,[14] Andresen *et al.*,[12] Drier and Wolfrum,[2] and Hall *et al.*[3] The energetics of reaction pathways have been the subject of theoretical studies by Melius and Binkley,[19] Abou-Rachid *et al.*,[20] and Phillips.[21]

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$NH_2 + NO_2 \rightarrow N_2O + H_2O \quad (1)$
$\rightarrow N_2 + H_2O_2 \quad (2)$

ΔH° (1) = −378 kJ mol^{-1}
ΔH° (2) = 355 kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.11 \pm 0.18) \times 10^{-11}$	297	Whyte and Phillips, 1983[1]	(a)
$(2.26 \pm 0.08) \times 10^{-11}$	298	Xiang, Torres, and Guillory, 1985[2]	(b)
Reviews and Evaluations			
$1.7 \times 10^{-11} (T/298)^{-2.2}$	250–500	CODATA, 1984[3]	(c)
$2.1 \times 10^{-12} \exp(650/T)$	200–300	NASA, 1985[4]	(d)
$2.1 \times 10^{-12} \exp(650/T)$	200–300	NASA, 1987[5]	(e)

Comments

(a) Laser flash photolysis of NH_3 at 193 nm. First-order decay of NH_2 monitored by laser induced fluorescence at 598 nm. Total pressure of 1–2 Torr.

(b) Infrared multiphoton dissociation of NH_3, CH_3NH_2, and N_2H_4. First order decay of state-selected NH_2 monitored by laser induced fluorescence at 533 nm. Total pressure of 2–10 Torr Ar. Also measured rate constant for reaction of vibrationally excited NH_2 and observed decrease of decay rate with vibrational excitation.

(c) Based on data of Hack *et al.*[6] and Kurasawa and Lesclaux.[7]

(d) Based on data of Hack *et al.*,[6] Kurasawa and Lesclaux,[7] and Whyte and Phillips.[1]

(e) Based on data of Hack *et al.*,[6] Kurasawa and Lesclaux,[7] Whyte and Phillips,[1] and Xiang *et al.*[2]

Preferred Values

$k = 1.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.9 \times 10^{-11} (T/298)^{-2.2}$cm^3 molecule^{-1} s^{-1}over range 250–500 K.

Reliability

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

$\Delta n = \pm 1.5$.

Comments on Preferred Values

The three room temperature values obtained by flash photolysis techniques (Kurasawa and Lesclaux,[7] Whyte and Phillips,[1] and Xiang *et al.*[2]) are in good agreement, while the result of Hack *et al.*[6] obtained in a discharge flow system is a factor of 2 lower. The preferred value at 298 K is the average of the four reported values. The same factor of 2 discrepancy between results of flow and flash techniques which has been observed for the $NH_2 + NO$ reaction rate also seems to apply to results for this rate, although there are fewer studies. The preferred temperature dependence is the average of the only two temperature dependencies reported,[6,7] which are not in good agreement. Hack *et al.*[6] using mass spectrometric analysis determined that the predominant reaction channel is channel (1) to give $N_2O + H_2O$ with at least 95% of the reaction proceeding by this channel.

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$2NO + O_2 \rightarrow 2NO_2$

$\Delta H = -114$ kJ mol^{-1}

Rate coefficient data

k/cm^6 molecule^{-2} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.1) \times 10^{-38}$	298	Stedman and Niki, 1973[1]	(a)
$(2.4 \pm 0.4) \times 10^{-38}$	298	Brobst and Allen, 1988[2]	(b)
$1.8 \times 10^{-47} \times T^{2.7} \exp(1600/T)$	226–758	Olbregts, 1985[3]	(c)
2.1×10^{-38}	298		
Reviews and Evaluations			
$3.3 \times 10^{-39} \exp(530/T)$	273–660	Baulch *et al.*, 1973[4]	(d)

Comments

(a) Photolysis of 1–100 ppm concentrations of NO_2 in air using NO/O_3 chemiluminescence detectors.

(b) Intracavity dye laser absorption spectroscopy system. Total pressure ranged from 3.9–7.4 Torr. $[NO]/[O_2] > 1000$. Production of NO_2 monitored at 610 nm.

(c) Static one liter reactor. Total pressure measured with differential micromanometer. Partial pressure of NO_2 measured in absorption at 436 nm. Pressure of O_2 and NO range up to 26 Torr. Non-Arrhenius behavior observed with k first decreasing with increasing temperature, reaching a minimum value at 600 K and then increasing with increasing temperature.

Preferred Values

$k = 2.0 \times 10^{-38}$ cm^{6}molecule^{-2}s^{-1} at 298 K.

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

Reliability

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

$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values

This evaluation accepts the recommendation given in the evaluation by Baulch *et al.*[1] The room temperature value has been confirmed by the newer studies, Olbregts[2] observed non-Arrhenius behavior over the entire temperature range studied and expressed k by the modified Arrhenius expression given here and also as the sum of two Arrhenius expressions. However, from 250 K to about 600 K his total rate coefficient is in good agreement with the value calculated from the expression recommended here. Olbregts interprets his results in terms of a multistep mechanism involving NO_3 or the dimer $(NO)_2$ as intermediates. For atmospheric modeling papers, the expression recommended here is adequate.

References

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$NO + NO_3 \rightarrow 2NO_2$

$\Delta H^\circ = -95$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.55 \pm 0.23) \times 10^{-11} \exp[(195 \pm 39)/T]$	209–299	Hammer, Dlugokencky, and Howard, 1986[1]	(a)
$(2.95 \pm 0.16) \times 10^{-11}$	299–414		
$(1.59 \pm 0.32) \times 10^{-11} \exp(122/T)$	224–328	Sander and Kircher, 1986[2]	(b)
$(2.41 \pm 0.48) \times 10^{-11}$	298		
Relative Rate Coefficients			
$(2 \pm 1) \times 10^{-11}$	298	Croce de Cobos, Hippler, and Troe, 1984[3]	(c)
Reviews and Evaluations			
2×10^{-11}	298	CODATA, 1984[4]	(d)
$1.3 \times 10^{-11} \exp(250/T)$	200–300	NASA, 1985[5]	(e)
$1.7 \times 10^{-11} \exp(150/T)$	200–300	NASA, 1987[6]	(f)

Comments

(a) Flow tube reactor. NO_3 detected by LIF in presence of excess NO. NO_3 produced by reaction $F + HNO_3$ and by thermal decomposition of N_2O_5. Nonlinear Arrhenius behavior over temperature range 209–414 K observed with constant value of rate coefficient above room temperature.

(b) Flash photolysis system with NO_3 decay in excess NO monitored in absorption at 661.8 nm. NO_3 produced by photolysis of Cl_2–$ClONO_2$ mixtures at wavelengths longer than 300 nm. Total pressure varied from 50–700 Torr He, N_2.

(c) Derived from numerical simulation of study of recombination reaction $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ at high pressures.

(d) Based on data of Graham and Johnston.[7]

(e) Based on unpublished data of Torabi[8] and preliminary data of Hammer *et al.*[1] (f) Based on unpublished data of Torabi,[8] Hammer *et al.*,[1] and Sander and Kircher.[2]

Preferred Values

$k = 2.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.6 \times 10^{-11} \exp(150/T)$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

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

Comments on Preferred Values

The preferred value of k(298 K) is taken as the average of the room temperature values reported by Hammer *et al.*,[1] and Sander and Kircher[2] which are in excellent agreement. The preferred temperature dependence is based on the data of Sander and Kircher[2] and that of Hammer *et al.*[1] below 300 K. Because of the non-Arrhenius behavior observed[1] above room temperature the range of validity of the preferred Arrhenius expression is restricted to 200–300 K.

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$NO_2 + O_3 \rightarrow NO_3 + O_2$

$\Delta H^\circ = -105$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.45 \pm 0.12) \times 10^{-17}$	296	Cox and Coker, 1983[1]	(a)
$(2.97 \pm 0.14) \times 10^{-13} \exp[-(2620 \pm 90)/T]$	277–325	Verhees and Adema, 1985[2]	(b)
Reviews and Evaluations			
$1.2 \times 10^{-13} \exp(-2450/T)$	230–360	CODATA, 1984[3]	(c)
$1.2 \times 10^{-13} \exp(-2450/T)$	230–360	NASA, 1985[4]	(c)
$1.4 \times 10^{-13} \exp(-2500/T)$	230–360	NASA, 1987[5]	(d)

Comments

(a) Static system. Experiments done both with NO_2 and with O_3 in excess. Time resolved absorption spectroscopy used to monitor N_2O_5 with a diode laser infrared source and NO_2 and O_3 at 350 and 255 nm, respectively, using conventional UV techniques. Total pressure was 10 Torr N_2. N_2O_5 was shown to be the only stable nitrogen-containing product. Overall stoichiometry for reactant decay (α) defined as $\Delta NO_3/\Delta O_3$ was determined to have value of 1.85 ± 0.09. Minor role for unsymmetrical NO_3 species suggested to account for stoichiometric factor having value less than 2.

(b) Continuous stirred tank reactor flow system. NO_2 and O_3 at sub-ppm concentration levels. Chemiluminescent analysis. Wall reactions were found to be very important. Relative humidity levels up to 80% did not affect the value of the rate constant.

(c) Based on data of Davis *et al.*,[6] Graham and Johnston,[7] and Huie and Herron.[8]

(d) Based on same data as cited in note (c). Value of activation energy rounded.

Preferred Values

$k = 3.2 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.2 \times 10^{-13} \exp(-2450/T)$ cm^3 molecule^{-1} s^{-1} over range 230–360 K

Reliability

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

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

Comments on Preferred Values

Preferred value is unchanged from the CODATA evaluation,[3] which was based on the data in the three temperature-dependent studies of Davis *et al.*,[6] Graham and Johnston,[7] and Huie and Herron.[8] The recent results of Cox and Coker[1] are in excellent agreement with this recommendation. The recent results of Verhees and Adema[2] show a similar temperature dependence but a higher preexponential factor. It was shown that wall reactions play an important role in this study. These results have not been included in the derivation of the preferred value, but may be considered to be in reasonable agreement with the recommendation.

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$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

$\Delta H^\circ = -94.7$ kJ mol^{-1}

Low-pressure rate coefficient

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.7 \pm 0.6) \times 10^{-30}(T/300)^{-3.4 \pm 1.3}$ [He]	236–358	Kircher, Margitan and Sander, 1984[1]	(a)
$(4.5 \pm 1.1) \times 10^{-30}/T/300)^{-3.4 \pm 1.3}$ [N_2]			
9.5×10^{-31} [He]	298	Smith, Ravishankara, and Wine, 1985[2]	(b)
2.1×10^{-30} [N_2]			
Reviews and Evaluations			
$(3.0 \pm 1.5) \times 10^{-30}$ [N_2]	298	Croce de Cobos, Hippler, and Troe, 1984[3]	(c)
$3.7 \times 10^{-30}(T/300)^{-4.1}$ [N_2]	220–300	CODATA, 1982[4]	(d)
$2.2 \times 10^{-30}(T/300)^{-4.3}$ [air]	200–300	NASA, 1987[5]	(e)

Comments

(a) Flash photolysis. Visible absorption of NO_3 monitored under pseudo-first order conditions. Falloff curve measured over the pressure range 20–700 Torr and extrapolated using reduced falloff curve representation with $F_c = 0.34$ at 298 K.

(b) Discharge flow-long path absorption technique. Visible absorption of NO_3 monitored. Pressure range 1–8 Torr in He, and 0.5–6 Torr in N_2. Reduced falloff curves extrapolated with $F_c = 0.47$ for N_2 at 298 K.

(c) Analysis of high pressure measurements of recombination (see high-pressure rate coefficients) and earlier low-pressure measurements of dissociation[6,7] converted using equilibrium constants). Reduced falloff representation from Ref. 9 employed with $F_c = 0.34$ at 298 K.

(d) From dissociation experiments[6,7] and equilibrium constant[8] using falloff analysis by Malko and Troe[9] with $F_c = 0.34$ at 298 K.

(e) Based on the data of Refs. 1–3, 6–12 using a standard value of $F_c = 0.6$ at 298 K. A smaller value of F_c would result in larger values of k_0 and k_∞.

Preferred Values

$k = 2.7 \times 10^{-30}(T/300)^{-3.4}$ [N_2] over the range 200–300 K.

Reliability

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

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The direct measurements of the falloff curve for recombination from Refs. 1–3, and 10–12 are all in very good agreement and well represented by the expression from Ref. 1 which was based on $F_c = 0.34$ and $k_\infty = 1.65\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. The differences in the extrapolated values of k_0 between the reviews in Refs. 3 and 4 and in Ref. 5 are due to the application of a standard value $F_c = 0.6$ in the latter evaluation whereas modeled smaller F_c values were employed in Refs. 1, 3, and 4.

High-pressure rate coefficients
Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.2\pm0.5)\times10^{-12}$	293	Croce de Cobos, Hippler, and Troe, 1984[3]	(a)
$(1.65\pm0.15)\times10^{-12}(T/300)^{-0.4\pm0.5}$	236–358	Kircher, Margitan, and Sander, 1984[1]	(b)
1.85×10^{-12}	298	Smith, Ravishankara, and Wine, 1985[2]	(c)
Reviews and Evaluations			
$1.6\times10^{-12}(T/300)^{0.2}$	220–520	CODATA, 1982[4]	(d)
$1.5\times10^{-12}(T/300)^{-0.5}$	200–300	NASA, 1987[5]	(e)

Comments

(a) Laser flash photolysis of N_2O in the presence of NO_2. NO_3 monitored by visible absorption under pseudo-first order conditions. Falloff curve measured over the pressure range 1–200 atm in N_2.

(b) See comment (a) for k_0.

(c) See comment (b) for k_0.

(d) Based on the analysis[9] of dissociation falloff curves from Refs. 6 and 7 and equilibrium constant K_c from Ref. 8.

(e) See comment (e) for k_0.

Preferred Values

$k_\infty = 2.0\times10^{-12}(T/300)^{0.2}$ cm^3 $molecule^{-1}$ s^{-1} over the range 200–500 K.

Reliability

$\Delta \log k_\infty$ ± 0.1.

$\Delta n = \pm 0.6$.

Comments on Preferred Values

The recommended value is based on the high-pressure measurements of the recombination which are consistent with the results in the falloff range from Refs. 1, 2, and 10–12 when a falloff representation with $F_c \approx 0.34$ is used. Increasing F_c to a standard value $F_c = 0.6$, such as done in the review of Ref. 5, would give less good agreement with the measurements at pressures above 5 atm, but represent the low-pressure data satisfactorily.

Intermediate falloff range
Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	P/Torr	M	Temp./K	Reference	Comments
Absolute Rate Coefficients					
4.8×10^{-13}	24	N_2	298	Burrows, Tyndall, and Moortgat, 1985[10]	(a)
5.8×10^{-13}	40				
5.6×10^{-13}	120	He	298	Wallington *et al.*, 1986[11]	(b)
8.0×10^{-13}	400				
4.0×10^{-13}	25	N_2	298	Wallington *et al.*, 1987[12]	(b)
7.0×10^{-13}	100				
4.5×10^{-13}	25	O_2			
8.8×10^{-13}	400				

Comments

(a) Photolysis of flowing Cl_2–$ClONO_2$–NO_2 mixtures (or F_2–$ClONO_2$–NO_2 mixtures). NO_3 monitored by visible absorption. Molecular modulation spectroscopy.

(b) Flash photolysis of F_2–HNO_3 mixtures or of $ClONO_2$. Detection of NO_3 by visible absorption in a long path cell. Efficiencies of N_2 and O_2 are identical within the experimental errors.

Temperature dependence of F_c

For molecules of the size of N_2O_5 a temperature dependence of F_c should be taken into account. The analysis in

Ref. 9 gave $F_c \approx \exp(-T/250) + \exp(-1050/T)$ with $F_c \approx 0.42$ at 220 K, 0.34 at 295 K, and 0.26 at 520 K. For a limited temperature and pressure range, the use of a standard value[5] of $F_c = 0.6$ would require a reduction of the apparent k_0 and k_∞ parameters in order to reproduce the experimental parts of the falloff curve.

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$N_2O_5 \rightleftarrows NO_2 + NO_3$

Comment

While measurements of N_2O_5 dissociation[1,2] and the reverse recombination[3] $NO_2 + NO_3 \rightarrow N_2O_5$ initially appeared consistent[4] with the equilibrium constant K_c from Graham and Johnston,[5] new determinations indicated larger discrepancies. An analysis of dissociation and recombination rates by Kircher, Margitan, and Sander[6] gave $K_c = 3.18 \times 10^{29}\ T^{-1} \exp(-11350/T)$ molecule cm^{-3} over the range 236–358 K with K_c (298 K) $= 3.1 \times 10^{10}$ molecule cm^{-3} whereas the Graham and Johnston[5] value was K_c (298 K) $= 4.3 \times 10^{10}$ molecule cm^{-3}. Measurements of the equilibrium concentrations (i) by Tuazon *et al.*[7] yield K_c (298 K) $= (2.91^{+0.89}_{-0.56}) \times 10^{10}$; (ii) by Perner *et al.*[8] yield K_c (298 K) $= 4.39 \times 10^{10}$, and (iii) by Burrows, Tyndall and Moortgat[9] yield $K_c = 1.23 \times 10^{28} \exp(-11960/T)$ corresponding to K_c (298 K) $= 4.6 \times 10^{10}$ molecule cm^{-3}. The most recent direct measurement of the equilibirum constant by Cantrell *et al.*[10] led to a low value of K_c (298 K) $= 2.25 \times 10^{10}$ and a temperature dependence of $K_c = 1.3 \times 10^{26} \exp(-10814/T)$ molecule cm^{-3}. A discussion of the various measurements of the equilibrium constant was given in Ref. 10 and by Johnston, Cantrell, and Calvert.[11] Obviously, the discrepancies in K_c (298 K) between 2.3 and 4.6×10^{10} molecule cm^{-3} are larger than the claimed experimental uncertainties.

In the kinetic measurements, the rates of the forward and reverse reactions should be compared along the falloff curve for the same bath gas and temperature. In the equilibrium concentration measurements, the uncertainties in some of the absorption coefficients are important. Presently, no recommendation, which is better than a factor of 2, can be made for the value of K_c.

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$N_2O_5 + H_2O \rightarrow 2HNO_3$

$\Delta H = -39.6$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$< 1.3 \times 10^{-21}$	298	Tuazon, *et al.*[1]	(a)
$< 1.5 \times 10^{-21}$	298	Atkinson, *et al.*[2]	(b)
$< 1.1 \times 10^{-21}$	296	Hjorth, *et al.*[3]	(c)
$< 3 \times 10^{-22}$	298	Sverdrup, *et al.*[4]	(d)
Reviews and Evaluations			
$< 2 \times 10^{-21}$	298	NASA, 1985[5]	(e)
$< 2 \times 10^{-21}$	298	NASA, 1987[6]	(f)

Comments

(a) N_2O_5 decay rates in two large volume (3800 and 5800 L) Teflon or Teflon-coated environmental chambers observed by FTIR absorption.

(b) Same as (a) except that a 2500-L Teflon chamber replaced the 3800-L Teflon chamber. Authors suggest that observed decay proceeds only by heterogeneous processes.

(c) N_2O_5 decay rates in a 1500-L FEP-Teflon bag observed by FTIR absorption.

(d) Large volume (17 300-L) Teflon-lined chamber. Concentration profiles for O_3, total nitrogen oxides and NO_2 were measured and were calculated for N_2O_5 and HNO_3. Results modeled with kinetic mechanism of eleven gas phase reactions and five heterogeneous reactions.

(e) Based on data of Tuazon *et al.*[1]

(f) Based on data of Tuazon *et al.*[1] and Hjorth *et al.*[3]

Preferred Values

$k < 2 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This upper limit is based on data of Tuazon *et al.*,[1] Atkinson *et al.*,[2] and Hjorth *et al.*[3]. It is possible that the observed decays proceed only by heterogeneous processes. While the lower value of Sverdrup *et al.*[4] may in fact be closer to the value of the rate coefficient for the homogeneous gas phase reaction, because it is less direct we prefer the more conservative recommendation given here.

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HONO + *hν*

Comment

Since the previous evaluation of the data for this process (Ref. 1), one paper with additonal information has been published. Kenner, Rohrer, and Stuhl[2] have studied the production of electronically excited OH(A) in the 193 nm photolysis of HONO and report a low quantum yield of about 10^{-5} for its production. They also studied the absorption spectrum in the wavelength region 185–270 nm and obtained results in good agreement with those of Cox and Derwent[3] over the 220–270 nm range but did not observe the peak at 215 nm reported in that study. The recommendations in reference 1 are for the wavelength region 300–400 nm and are unchanged.

References

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$HONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH_0° /kJ mol^{-1}	λ threshold/nm
$HONO_2 + h\nu \rightarrow HO + NO_2$	(1)	200	598
$\rightarrow HONO + O(^3P)$	(2)	298	401
$\rightarrow H + NO_3$	(3)	418	286
$\rightarrow HONO + O(^1D)$	(4)	488	245

Absorption cross section data

Wavelength range/nm	Reference	Comment
110–190	Okabe, 1980[1]	(a)
105–220	Suto and Lee, 1984[2]	(b)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comment
$\phi_2 = 0.03$	266	Margitan and Watson, 1982[3]	(c)
$\phi_3 < 0.002$	266		
$\phi_1 = 0.89 \pm 0.08$	222	Jolly *et al.*, 1986[4]	(d)

Comments

(a) Measured at 298 K with spectral resolution of 0.1–0.3 nm. Fluorescence from $HO(^2\Sigma)$ observed only below 147.5 nm. The vibrational and rotational distributions of $HO(^2\Sigma)$ produced from photolysis at 123.6 nm were measured.

(b) Measured at 298 K with spectral resolution of 0.23 nm. Fluorescence from $HO(^2\Sigma)$ observed below 153 nm, fluorescence cross sections measured.

(c) Flash photolysis–resonance fluorescence technique. Photolysis with a frequency quadrupled Nd:YAG laser. HO observed in fluorescence at 309 nm. O atoms and H atoms looked for directly using atomic resonance fluorescence.

(d) Pulsed laser photolysis with a KrCl excimer laser. HO detected by timeresolved resonance absorption at 308.3 nm. Error estimate quoted does not include the uncertainty of + 17%, − 8% resulting from an analysis of potential systematic errors.

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
190	1560	260	1.88
195	1150	265	1.71
200	661	270	1.59
205	293	275	1.35
210	105	280	1.10
215	35.6	285	0.85
220	15.1	290	0.61
225	8.62	295	0.41
230	5.62	300	0.24
235	3.72	305	0.15
240	2.57	310	0.07
245	2.10	315	0.03
250	1.91	320	0.01
255	1.90	325	0.00

Quantum yields

$\phi_1 = 1.0$ throughout this wavelength region

Comments on preferred values

The preferred absorption cross section values are those of Molina and Molina.[5] They are in good agreement with the results of Johnston and Graham[6] except at both ends of the wavelength region covered where they agree better with results reported by Biaume.[7] The preferred value of the quantum yield is based on the results of Johnston *et al.*[8] and the recent direct observations of Jolly *et al.*[4] The absence of the competing processes (2) and (3) is shown by the direct observations of Margitan and Watson.[3] Jacobs *et al.*[9] observed no vibrational and little rotational excitation of the HO produced by photodissociation at 193 nm. Kenner *et al.*[10] have proposed a two-photon process for excitation of electronically excited HO(A) in the 193 nm ArF excimer laser photolysis of nitric acid.

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$HO_2NO_2 + h\nu$

Comment

Since the previous evaluation of the data for this process (Ref. 1), there has been one experimental study and one theoretical study of the photodissociation of HO_2NO_2. MacLeod, Smith, and Golden[2] studied the photodissociation at 248 nm using a very low pressure photolysis system with a KrF excimer laser. HO radicals were monitored by LIF, and the quantum yield for production of HO was determined to be 34 ± 16%. A broadband fluorescence emission spectrum was observed and attributed to electronically excited NO_2. A maximum yield of 30% for NO_2^* production was determined. Saxon and Liu[3] reported a theoretical study of the ground state and excited states of HO_2NO_2. They proposed that photolysis results in removal of an oxygen atom or an oxygen molecule from the NO_2 end of the molecule. These new results provide the only data on the photodissociation mechanism, and until they are confirmed, we prefer to make no recommendation for primary quantum yields. The preferred cross section values which are those of Molina and Molina[4] are unchanged from the previous evaluation.[1]

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$NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°$/kJ mol^{-1}	λ threshold/nm
$NO_2 + h\nu \rightarrow NO + O(^3P)$ (1)	300	398
$\rightarrow NO + O(^1D)$ (2)	490	244

Absorption cross section data

Wavelength range/nm	References	Comment
200–700	Schneider *et al.*, 1987[1]	(a)
427–450	Leroy, Rigaud, and Hicks, 1987[2]	(b)
391–414	Koffend *et al.*, 1987[3]	(c)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comment
ϕ_1	334–404	Gardner, Sperry and Calvert, 1987[4]	(d)

Comments

(a) Measured at 298 K with spectral resolution of 0.04 nm. Averaged values over 1 nm intervals are tabulated. Also averaged values over 5 nm intervals are tabulated and compared with corresponding values derived from previous studies. Generally good agreement with results of Bass *et al.*[5] except for higher values near the absorption minimum at 260 nm and at wavelengths less than 220 nm.

(b) Measured at 198 and 235 K with spectral resolution of 0.04 nm. Values tabulated at 0.1 nm intervals. The relative reduction in cross section values at the lower temperature was observed to be substantially greater at the absorption minima (15%–20%) than at the wavelengths of maximum absorption, where it was only 3%–4%.

(c) Measured at 300 K with spectral resolution of 0.005 nm for several selected narrow wavelength intervals within this spectral range. Above 410 nm measurements were also made at 252 K with only slight variation of some features observed.

(d) Primary quantum yield ϕ_1 derived from measurement of (1) quantum yield of NO_2 reactant loss (optical absorption); (2) quantum yield of NO product formation (mass spectrometry); and (3) quantum yield of O_2 product formation (mass spectrometry). Light intensity measured by NOCl actinometry. ϕ_1 found to be near unity for wavelengths less than 394 nm. At 404 nm measurements also made from 273 K to 370 K. Results found to be in qualitative agreement with the simple theory that for $\lambda > 398$ nm the energy deficiency for photodissociation is made up for from internal rotational and vibrational energy of the NO_2 molecules. On the basis of later experiments in the same laboratory, Calvert *et al.*,[9] in which the absorption cross section at 404.7 nm was measured from 273 to 370 K, the authors concluded that vibrationally excited NO_2 molecules absorb more strongly than unexcited molecules. They were thereby able to derive a reasonable fit to the variation of primary quantum yield with temperature for photodecomposition in the energy-deficient region at 404.7 nm.

Preferred Values

Absorption Cross Section

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
185	26.0	245	4.3	305	16.6	365	57.8
190	29.3	250	2.8	310	17.6	370	54.2
195	24.2	255	1.4	315	22.5	375	53.5
200	25.0	260	1.9	320	25.4	380	59.9
205	37.5	265	2.0	325	27.9	385	59.4
210	38.5	270	3.1	330	29.9	390	60.0
215	40.2	275	4.0	335	34.5	395	58.9
						400	67.6
220	39.6	280	5.5	340	38.8	405	63.2
225	32.4	285	7.0	345	40.7	410	57.7
230	24.3	290	8.2	350	41.0		
235	14.8	295	9.7	355	51.3		
240	6.7	300	11.7	360	45.1		

Quantum yields

λ/nm	ϕ_1	λ/nm	ϕ_1	λ/nm	ϕ_1	λ/nm	ϕ_1
<310	1.00	355	0.99	394	0.95	412	0.09
315	0.99	360	0.98	396	0.92	414	0.07
320	0.99	365	0.98	398	0.82	416	0.05
325	0.99	370	0.98	400	0.69	418	0.03
330	0.99	375	0.98	402	0.56	420	0.02
335	0.99	380	0.97	404	0.42	422	0.01
340	0.99	385	0.97	406	0.29	424	0.00
345	0.99	390	0.96	408	0.18		
350	0.99	392	0.96	410	0.13		

Comments on preferred values

The preferred absorption cross section values are those of Bass *et al.*[5] The absorption spectrum is highly structured; for greater detail and in order to calculate values averaged over appropriate wavelength intervals, the reader should consult Ref. 5 where values are tabulated every 1/8 th nm. They are in generally good agreement with the new results of Schneider *et al.*[1] except for unexplained differences of as much as 20%–25% near the absorption minimum at 260 nm and at wavelengths less than 220 nm. The preferred quantum yield values are those recommended in Gardner *et al.*[4] They are based on a best fit to the data of Gardner *et al.*[4] from 334 to 404 nm, Jones and Bayes[6] for 297–412 nm, Davenport[7] for 400–420 nm, and Harker *et al.*[8] (corrected for cross sections) for 397–420 nm. The results of Gardner *et al.*[4] support the results of Jones and Bayes[6] showing that the primary quantum yield is nearly unity throughout the entire wavelength region from 290 to 390 nm, and that the low values reported by Harker *et al.*[8] for the 375–396 nm region must be in error. Possible reasons for these low values are discussed in Ref. 4.

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$NO_3 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°$/kJ mol^{-1}	λ threshold/nm
$NO_3 + h\nu \rightarrow NO + O_2$ (1)	13	9000
$\rightarrow NO_2 + O$ (2)	206	580

Absorption cross section data

Wavelength range/nm	References	Comment
613–672	Marinelli, Swanson, and Johnston, 1982[1]	(a)
565–673	Ravishankara and Wine, 1983[2]	(b)
662	Cox *et al.*, 1984[3]	(c)
615–670	Burrows, Tyndall, and Moortgat, 1985[4]	(d)
652–672	Ravishankara and Mauldin, 1986[5]	(e)
400–700	Sander, 1986[6]	(f)
600–700	Cantrell *et al.*, 1987[7]	(g)
662	Canosa-Mas *et al.*, 1987[8]	(h)

Comments

(a) *NO_3 from NO_2+O_3.* Measured cross sections scaled by factor 1.17 needed to bring integrated absorption in 662 nm band into agreement with literature value.

(b) *NO_3 from $F+HNO_3$.* NO_3 concentration determined by titration with NO. From the 662 nm band, integrated absorption of 1.88×10^{-15} cm and peak cross section value of 1.78×10^{-17}cm^2 reported.

(c) *NO_3 from photolysis of Cl_2 in $ClONO_2$.* Cross section value at 662 nm of 1.63×10^{17} cm^2 reported.

(d) *NO_3 from photolysis of Cl_2–$ClONO_2$ or F_2–HNO_3 mixtures.* For 662 nm band, integrated absorption of 1.82×10^{-15} cm and peak cross section value of 1.85×10^{-17} cm^2 reported.

(e) *NO_3 from $F+HNO_3$ in discharge flow apparatus.* Measurements made at 220, 240, and 298 K. For the 662 nm band at 298 K, integrated absorption of 1.94×10^{-15} cm and peak cross section value of 1.90×10^{-17} cm^2 reported. Absorption cross section at 662 nm found to increase with decreasing temperature while the shape of the band did not change.

(f) *Two methods used to produce NO_3.* Flash photolysis method used photolysis of Cl_2–$ClONO_2$ mixtures and monitored NO_3 formation and $ClONO_2$ disappearance by UV absorption. Measurements made at 230, 250 and 298 K. Derived value of σ (NO_3) at 662 nm determined by this method (2.28×10^{-17} cm^2) preferred by the author. Cross section found to increase by factor of 1.18 at 230 K. NO_3 also produced in discharge flow system by reaction of F atoms with HNO_3. The value of σ (NO_3) at 662 nm determined by this method was 1.83×10^{-17} cm^2. Values of σ tabulated for each nanometer from 400–700 nm for 298 K and 230K.

(g) *NO_3 from $NO+O_3$.* Method used was Fourier Transform spectroscopy in the visible and infrared spectral regions over the temperature range from 215 to 348 K. For the 662 nm band, integrated absorption of 2.05×10^{-15} cm and peak cross section value of 2.09×10^{-17} cm^2 reported. No dependence on temperature was observed.

(h) *NO_3 from $F+HNO_3$ in discharge flow apparatus.* NO_3 concentration determined by titration with NO and stoichiometric factor determined. Absorption cross section of NO_3 at 662 nm determined to be 2.23×10^{-17} cm^2.

Preferred Values

Absorption cross sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
650	50	661	1320
651	53	662	2020
652	56	663	1760
653	62	664	1120
654	77	665	760
655	94	666	468
656	133	667	257
657	174	668	165
658	224	669	114
659	360	670	86
660	665		

Quantum yields
No recommendation

Comments on preferred values

The preferred absorption cross section values have been adopted from the evaluation NASA, 1987.[a] They are based on the results of Ravishankara and Wine[2], and those of

Sander.[6] Effects of secondary chemistry were minimized in these studies. The recommendation is supported by the new results in Cantrell *et al.*[7] and Canosa-Mas *et al.*[8] The shape of the 662 nm absorption band as tabulated by Sander[6] is in good agreement with that of Marinelli *et al.*[1] Conflicting results have been reported regarding the effect of temperature on the value of the absorption cross section Ravishankara and Mauldin[5] and Sander[6] have reported a significant increase in the value of $\sigma(NO_3)$ at 662 nm at lower temperatures while Cantrell *et al.*[7] report no temperature dependence from 215 to 348 K. This discrepancy needs to be resolved.

No recommendation for absolute quantum yields is given. As discussed in the previous CODATA evaluation,[10] the primary quantity determined by Magnotta and Johnston[11] was the product of the absorption cross section times the quantum yield. However, these values yield quantum yield values greater than unity for $\lambda < 610$ nm, indicating some systematic error. The recommendation is to use the photodissociation rates suggested by Magnotta and Johnston for an overhead sun at the earth's surface and the wavelength range 470 to 700 nm: $J_1(NO + O_2) = 0.022 \pm 0.007\ s^{-1}$ and $J_2(NO_2 + O) = 0.18 \pm 0.06\ s^{-1}$.

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$N_2O + h\nu \rightarrow$ products

Comment

Since the previous evaluation of the data for this process (Ref. 1), three papers with additional information have been published. Selwyn and Johnston[2] have studied the ultraviolet absorption spectrum of nitrous oxide and its ^{15}N isotopes over the wavelength range 172–197 nm and the temperature range 150–500 K. Lee and Suto[3] have measured the photoabsorption and fluorescence cross sections in the 105–160 nm region and studied the production and quenching of excited photofragments. Yoshino, Freeman, and Parkinson[4] have made high resolution, room temperature cross section measurements in the 170–222 nm range. The new results are in good agreement with the recommendations in Ref. 1, which are therefore left unchanged.

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$N_2O_5 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_0/kJ mol^{-1}	λ threshold/nm
$N_2O_5 + h\nu \rightarrow NO_3 + NO_2$	(1)	89	1340
$\rightarrow NO_3 + NO + O$	(2)	390	307
$\rightarrow NO_3 + NO_2^* \rightarrow NO_3 + NO_2 + h\nu$	(3)		

Absorption cross section data

Wavelength range/nm	References	Comment
200–380	Yao, Wilson, and Johnston, 1982[1]	(a)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comment
$\phi(NO_3)$	249–350	Swanson, Kan, and Johnston, 1984[2]	(b)
$\phi(NO_3)$, $\phi[O(^3P)]$	290	Barker *et al.*, 1985[3]	(c)
$\phi(NO_3)$, $\phi[O(^3P)]$	248–289	Ravishankara *et al.*, 1986[4]	(d)
ϕ_3	266–305	Oh *et al.*, 1986[5]	(e)

Comments

(a) Measured for 223–300 K. For 200–280 nm no temperature dependence was observed, and values are tabulated at 5 nm intervals. For 285–380 nm a pronounced temperature dependence was observed and results are presented by equation expressing σ as a function of λ and T.

(b) Laser flash photolysis mostly at 249 nm with a few experiments at 350 nm. NO_3 detected by laser resonance absorption at 662 nm. Average NO_3 quantum yield = 0.89 ± 0.15. At low reactant concentration, quantum yield approached a value of 1.0 ± 0.1.

(c) Pulsed laser photolysis. Quantum yield for production of $O(^3P)$ determined to be $\leqslant 0.1$ in experiments with resonance fluorescence detection of oxygen atoms. Optoacoustic techniques with added NO were used to determine $\phi(NO_3)$ to be 0.8 ± 0.2.

(d) Pulsed laser photolysis. Quantum yield for NO_3 production at 248 nm determined to be unity in experiments with detection of NO_3 in absorption at 662 nm. Quantum yield for $O(^3P)$ production determined by resonance fluorescence to decrease from 0.72 ± 0.17 at 248 nm to 0.15 ± 0.05 at 289 nm.

(e) Pulsed laser photolysis. The photolysis induced fluorescence, PIF, of NO_2 compared with the laser induced fluorescence, LIF, of NO_2 excited by a pulsed visible laser. Analysis of results indicate that electronically excited NO_2 in the $^2B_1$ state is produced in the UV photolysis of N_2O_5.

Preferred Values

Absorption cross sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
200	920	245	52
205	820	250	40
210	560	255	32
215	370	260	26
220	220	265	20
225	144	270	16
230	99	275	13
235	77	280	12
240	62		

For 285–380 nm and 225–300 K use formula: $10^{20}\sigma = \exp[2.735 + (4728 - 17.13\,\lambda)/T]$

Quantum yields
$\phi_1 + \phi_2 + \phi_3 = 1.0$ for λ = 248–350 nm

λ/nm	ϕ_2
248	0.72 ± 0.17
266	0.38 ± 0.10
287	0.21 ± 0.05
289	0.15 ± 0.05

Comments on preferred values

The preferred absorption cross section values are those of Yao *et al.*[1] For wavelengths less than 280 nm no significant temperature dependence was observed, and for this region the preferred values are tabulated. For the region 285–380 nm there is a significant temperature dependence, and the preferred values must be calculated from the expression given. These results agree well with the room temperature values for 210–310 nm reported by Graham and Johnston.[6] The preferred quantum yield of unity for NO_3 production is based on the results of Swanson *et al.*[2] at 249 and 350 nm, those of Ravishankara *et al.*[4] at 248 nm, and those of Barker *et al.*[3] at 290 nm. The preferred quantum yield values for O atom production are those reported by Ravishankara *et al.*[4] The recent study of Oh *et al.*[5] indicates that electronically excited NO_2 in the $^2B_1$ state is produced and photolysis induced fluorescence (PIF) quantum yield values are reported. For calculation of photodissociation rates in the atmosphere (3) is equivalent to (1). In summary it appears that NO_3 is produced with unit quantum yield throughout the region 248–350 nm, and that the quantum yield for oxygen atom production decreases at longer wavelengths and appears to be approaching zero in the neighborhood of the thermodynamic threshold for O atom production at 307 nm.

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4.4. Organic Species

$O + CH_3 \rightarrow HCHO + H$

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

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.4 \pm 0.3) \times 10^{-10}$	294–900	Slagle, Sarzynski, and Gutman, 1987[1]	(a)
Reviews and Evaluations			
1.1×10^{-10}	200–300	CODATA, 1984[2]	(b)
1.1×10^{-10}	200–300	NASA, 1985[3]	(c)
1.1×10^{-10}	200–300	NASA, 1987[4]	(c)

Comments

(a) Flow system with generation of CH_3 and $O(^3P)$ from simultaneous *in situ* photolysis of CH_3COCH_3 and SO_2, and determination of $[CH_3]$ and $[O]$ by photoionization mass spectrometry. Experiments were performed under conditions such that $[O]/CH_3] > 20$, and rate coefficients were determined from decay of CH_3. k found to be independent of pressure over range 1–11 Torr. k confirmed by measurements of rate of formation of HCHO, the sole observable product.

(b) Based on data of Plumb and Ryan.[5]

(c) Weighted average of measurements of Washida and Bayes.[6] Washida,[7] and of Plumb and Ryan.[5]

Preferred Values

$k = 1.4 \times 10^{-10}$ cm^3 molecule s^{-1} over range 200–900 K.

Reliability

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

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

Comments on Preferred Values

The recommended rate coefficient is taken from the recent extensive study by Slagle *et al*,[1] which confirms a temperature-independent k, which is in good agreement with the previous recommendations.[2–4]

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$O(^1D) + CH_4 \rightarrow HO + CH_3$ (1)
$\rightarrow O(^3P) + CH_4$ (2)
$\rightarrow HCHO + H_2$ (3)

Comment

A recent study[1] of the 248 nm laser flash photolysis 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 $v = 4$, the maximum allowable according to the energetics of the reaction) is non statistical.

The previous recommendations[2] for the rate coefficient ($k = k_1 + k_2 + k_3$) and the branching ratios k_1/k, k_2/k, and k_3/k are unchanged.

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$HO + CH_4 \rightarrow H_2O + CH_3$

$\Delta H^\circ = -60.7$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.7 \times 10^{-11} \exp(-2550/T)$	298–1229	Jonah, Mulac and Zeglinski, 1984[1]	(a)
7.48×10^{-15}	298		
$(2.6^{+9.7}_{-2.1}) \times 10^{-17} T^{1.83 \pm 0.17}$ $\times \exp[-(1396 \pm 134)/T]$	298–1512	Madronich and Felder, 1985[2]	(b)
$(8.5 \pm 0.6) \times 10^{-15}$	298		
Reviews and Evaluations			
$2.4 \times 10^{-12} \exp(-1710/T)$	200–300	CODATA, 1984[3]	(c)
$2.7 \times 10^{-18} T^{2.1} \exp(-1240/T)$	300–2200	Warnatz, 1984[4]	(d)
$2.4 \times 10^{-12} \exp(-1710/T)$	240–373	NASA, 1985[5]	(e)
$6.95 \times 10^{-18} T^2 \exp(-1280/T)$	240–1250	Atkinson, 1986[6]	(f)
$2.5 \times 10^{-18} T^{2.13} \exp(-1230/T)$	230–2000	Baulch *et al.*, 1986[7]	(g)
$3.2 \times 10^{-19} T^{2.4} \exp(-1060/T)$	240–2000	Tsang and Hampson, 1986[8]	(h)
$2.3 \times 10^{-12} \exp(-1700/T)$	240–373	NASA, 1987[9]	(e)

Comments

(a) Pulsed radiolysis-resonance absorption detection of HO.

(b) Flash photolysis-resonance fluorescence detection of HO.

(c) Derived from the absolute rate coefficient data of Davis *et al.*,[10] which are consistent with the rate coefficient data of Greiner,[11] Margitan *et al.*,[12] Zellner and Steinert,[13] Tully and Ravishankara,[14] Jeong and Kaufman,[15] Husain *et al.*,[16] and Baulch *et al.*[17]

(d) Derived from the absolute rate coefficients of Tully and Ravishankara.[14]

(e) Derived from the absolute rate coefficient data of Davis *et al.*,[10] which are in agreement with other temperature dependence studies.[11–15]

(f) Derived from the absolute rate coefficient data of

Greiner,[11] Davis *et al.*,[10] Margitan *et al.*,[12] Overend *et al.*,[18] Howard and Evenson,[19] Tully and Ravishankara,[14] Jeong and Kaufman[15] and Madronich and Felder.[2] [The data of Davis *et al.*[10] were recalculated, and the corrected data of Jeong and Kaufman[20] were used.] The rate coefficients at temperatures <1250 K were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$.

(g) Derived from the absolute rate coefficients of Greiner,[11,12] Wilson and Westenberg,[22] Davis *et al.*,[10] Margitan *et al.*,[12] Overend *et al.*,[18] Howard and Evenson,[19] Zellner and Steinert,[13] Sworski *et al.*,[23] Tully and Ravishankara,[14] Husain *et al.*[16] Jeong and Kaufman,[15] Cox *et al.*,[24] Peeters and Mahnen,[25] Ernst *et al.*,[26] and Dixon-Lewis and Williams,[27] using the three parameter equation $k = CT^n \exp(-D/T)$.

(h) Accepts the evaluation of Cohen and Westberg,[28] which was derived from the absolute rate coefficients of Refs. 10–15, 18, 19, 22 24 26 29, and 30 using the three parameter equation $k = CT^n \exp(-D/T)$.

Preferred Values

$k = 8.3\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.7\times10^{-12} \exp(-1820/T)$ cm^3 molecule^{-1} s^{-1} over the range 240–300 K.

Reliability of Preferred Values

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

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

Comments on Preferred Values

At room temperature and below, the absolute rate coefficients of Greiner,[11] Davis *et al.*,[10] Margitan *et al.*,[12] Overend *et al.*,[18] Howard and Evenson,[19] Zellner and Steinert,[13] Tully and Ravishankara,[14] Husain *et al.*,[16] Jeong and Kaufman,[15] Jonah *et al.*[1] and Madronich and Felder[2] are in good agreement. However, at higher temperatures there are discrepancies between the rate coefficients determined by Zellner and Steinert[13] (above ~625 K) and Jonah *et al.*[1] (400–600 K) and those of Greiner,[11] Margitan *et al.*,[12] Tully and Ravishankara,[14] Jeong and Kaufman,[15] Madronich and Felder[2] and Baulch *et al.*[17] (see Ref. 6).

The preferred values are derived from the absolute rate coefficient data of Refs. 2, 10–12, 14–16, 18, and 19. The three parameter equation $k = CT^2 \exp(-D/T)$ was fitted to these data, resulting in $k = 7.04\times10^{-18}\ T^2 \exp(-1286/T)$ cm^3 molecule^{1} s^{-1} over the range 240–1512 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 preferred rate coefficients over the range 240–300 K are uniformly ~10% higher than those given by the recent Baulch *et al.*[7] evaluation.

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

$\Delta H^\circ = -126$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6 \pm 3) \times 10^{-30}$ [He]	298	Hack *et al.*, 1983[1]	(a)
$(2.5 \pm 0.3) \times 10^{-30}$ [Ar]	295	Schmidt *et al.*, 1985[2]	(b)
5×10^{-30} [N_2]	298	Wahner and Zetzsch, 1985[3]	(c)
Reviews and Evaluation			
$2 \times 10^{-29}(T/300)^{-1.3}$ [N_2]	200–300	CODATA, 1984[4]	(d)
$5.5 \times 10^{-30}(T/300)^{0.0}$ [air]	200–300	NASA, 1987[5]	(e)
$5.6 \times 10^{-30}(T/300)^{0.0}$	228–300	Smith, Fairchild, and Crosley, 1984[11]	(f)

Comments

(a) Discharge flow system with ESR detection of HO radicals and mass spectrometric product identification. See comment in Ref. 4.

(b) Flash photolysis of H_2O_2 (or HNO_3) mixtures with C_2H_2. LIF detection of HO radicals near 300 nm. Experiments in He, Ar, and N_2 at pressures between 1 and 1000 mbar (in Ar). Construction of falloff curve with $F_c = 0.6$ and $k_\infty = (8.3 \pm 0.8) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. In the presence of O_2, glyoxal and vinoxy radicals were detected while HO radicals were regenerated. A mechanism

$$HO + C_2H_2 \rightarrow C_2H_2OH \xrightarrow{+O_2} (CHO)_2 + HO,$$

and

$C_2H_2OH \rightarrow CH_2CHO \xrightarrow{+O_2} (CHO)_2 + HO$ was postulated.

(c) Flash photolysis of H_2O_2 (or H_2O) mixtures with C_2H_2. Long path absorption detection of HO radicals. Experiments in N_2 over the range 20–1000 mbar. Falloff curve constructed with $F_c = 0.6$ and $k_\infty = 9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(d) Based on data from Ref. 1 and the NASA evaluation from 1983[5] using $F_c = 0.5$ and $k_\infty = 7.3 \times 10^{-13}$ cm^3 molecule^{-1}s^{-1}.

(e) Based on data from Refs. 7–10 using $F_c = 0.6$.

(f) Theoretical evaluation of the data from Refs. 9 and 10 using $F_c = 0.65$ and k_∞ (300 K) $= 8.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Simulation of k_0 up to temperatures of 1400 K.

Preferred Values

$k = 5 \times 10^{-30}(T/300)^{0.0}$ [N_2] cm^3 molecule^{-1} s^{-1} over the range 220–300 K.

Reliability

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

$\Delta n = +1$.

Comments on Preferred Values

The extrapolation of the falloff curve to the low pressure limit can now be made more safely than in our previous evaluation. The experimental data from Refs. 2 and 3, together with earlier results, give a consistent picture, in agreement with simulations of the falloff curve such as elaborated in Ref. 11.

High-pressure rate coefficient
Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.8 + 1.4) \times 10^{-13}$	298	Atkinson and Aschmann, 1984[12]	(a)
$(8.3 \pm 0.8) \times 10^{-13}$	295	Schmidt *et al.*, 1985[2]	(b)
9×10^{-13}	298	Wahner and Zetzsch, 1985[3]	(b)
$(8.8 \pm 2.0) \times 10^{-13}$	297	Hatakeyama, Washida and Akimoto, 1986[12]	(c)
Reviews and Evaluations			
6.5×10^{-12} e×p$(-650/T)$	200–300	CODATA, 1984[4]	(b)
7.3×10^{-13}	298		
$8.3 \times 10^{-13}(T/300)^{+2}$	200–300	NASA, 1987[6]	(b,d)

Comments

(a) HO radicals generated in the photolysis of CH_3ONO-NO-C_2H_2cyclohexane-air mixtures. Rates measured relative to the reaction HO + cyclohexane. Data evaluated using k(HO + cyclohexane) $= 7.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Measurements at 1 atm under the assumption that the high pressure limit is obtained.

(b) See comments for k_0.

(c) Generation of HO radicals by photolysis of H_2O_2 or ethylnitrites. Reactant and product concentrations monitored by long path FTIR spectrometry. Measurements at 1 atm in air. Reaction mechanism in the presence of O_2 in accord with Ref. 2.

(d) Based on simulation in Ref. 11.

Preferred Values

$k = 8.3\times10^{-13}(T/300)^{+2}$ cm^3 molecule^{-1} s^{-1} over the range 220–300 K.

Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Values

There is quite good agreement in the extrapolated high-pressure rate coefficients. The temperature coefficient of k_∞ corresponds to a small barrier for the addition reaction. Abstraction processes appear totally negligible at $T \leqslant 300$ K. For a simulation of the T and P dependence of the addition and abstraction pathways, see Ref. 11.

Intermediate Falloff Range

The measured falloff curves were evaluated with $F_c \approx 0.6$. The temperature dependence of F_c has been modelled in Ref. 11, leading to values of $F_c \approx 0.69$ at 228 K, 0.62 at 298 K, 0.43 at 600 K, and 0.31 at 1000 K.

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

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

Comments

New measurements, at 1 atm of synthetic air, of this reaction, generating HO radicals by flash photolysis of H_2O or HNO_3 and detecting HO by LIF, have been reported in Ref. 1. Pulse radiolysis experiments in Ref. 2 at 1 atm of Ar over the temperature range 340–560 K led to a negative temperature coefficient of the rate coefficient. This behavior, however, most probably is due to the onset of falloff effects at temperatures above 300 K. Since the new measurements for 300 K agree well with our earlier recommendation,[3] there is no change in the recommended value.

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$HO + C_2H_6 \rightarrow H_2O + C_2H_5$

$\Delta H^\circ = -80.1$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
8.0×10^{-14}	238	Margitan and Watson, 1982[1]	(a)
$(1.80\pm0.25)\times10^{-11}\exp[-(1240\pm110/T]$	240–295	Smith *et al.*, 1984[2]	(a)
$(2.63\pm0.10)\times10^{-13}$	295		
2.75×10^{-13}	295	Devolder *et al.*, 1984[3]	(b)
$(6.11\pm0.60)\times10^{-12}\exp[-(886\pm35)/T]$	248–472	Jeong *et al.*, 1984[4]	(b)
$(3.06\pm0.21)\times10^{-13}$	298		
$(2.2\pm0.3)\times10^{-13}$	295	Schmidt *et al.*, 1985[5]	(c)
$(2.67\pm0.40)\times10^{-13}$	295	Baulch, Campbell and Saunders, 1985[6]	(b)
$8.51\times10^{-18}T^{2.06}\exp(-430/T)$	293–705	Tully *et al.*, 1986[7]	(d)
$(2.39\pm0.21)\times10^{-13}$	293		
$(2.98\pm0.21)\times10^{-13}$	295	Nielsen *et al.*,1986[8]	(e)
$(1.28\pm0.09)\times10^{-13}$	248	Stachnik, Molina and Molina, 1986[9]	(f)
$(2.51\pm0.06)\times10^{-13}$	297		
$(8.4\pm3.1)\times10^{-12}\exp[-(1050\pm100)/T]$	226–363	Wallington, Neuman and Kurylo, 1987[10]	(a)
$(2.30\pm0.26)\times10^{-13}$	296		
$(2.74\pm0.3)\times10^{-13}$	296	Bourmada, Lafage and Devolder, 1987[11]	(b)
$(2.61\pm0.13)\times10^{-13}$	296	Zabarnick, Fleming and Lin, 1988[12]	(d)
Relative Rate Coefficients			
$(3.3\pm0.6)\times10^{-13}$	296	Edney, Kleindienst and Corse, 1986[13]	(g)
Reviews and Evaluations			
$1.9\times10^{-11}\exp(-1260/T)$	295–500	CODATA, 1984[14]	(h)
$1.1\times10^{-11}\exp(-1090/T)$	248–800	NASA, 1985[15]	(i)
$1.37\times10^{-17}T^2\exp(-444)/T$	238–800	Atkinson, 1986[16]	(j)
$2.3\times10^{-11}\exp(-1340/T)$	250–1200	Baulch *et al.*, 1986[17]	(k)
$1.47\times10^{-17}T^{1.04}\exp(-913/T)$	300–2000	Tsang and Hampson, 1986[18]	(l)
$1.1\times10^{-11}\exp(-1100/T)$	248–800	NASA, 1987[19]	(m)

Comments

(a) Flash photolysis–resonance fluorescence detection of HO.

(b) Discharge flow–resonance fluorescence detection of HO.

(c) Laser photolysis–laser induced fluorescence detection of HO in 1 atm total pressure of air diluent.

(d) Laser photolysis–laser induced fluorescence detection of HO.

(e) Pulsed radiolysis–resonance absorption detection of HO.

(f) Laser photolysis–resonance absorption detection of HO.

(g) Relative rate method. HO radicals generated by photolysis of CH_3ONO–NO–air mixtures at 1 atm total pressure. C_2H_6 decay measured relative to that for propane and the relative rate coefficient placed on an absolute basis using $k(OH + C_3H_8) = 1.14 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[16]

(h) The room-temperature absolute rate coefficients of Greiner,[20] Overend *et al.*,[21] Howard and Evenson,[22] Leu,[23] Lee and Tang,[24] and Tully *et al.*[25] were used to derive the 298 K rate coefficient. The temperature dependence was derived from the data of Greiner[20] and Tully *et al.*[25]

(i) The room-temperature absolute rate coefficients of Greiner,[20] Overend *et al.*,[21] Howard and Evenson,[22] Leu,[23] Lee and Tang,[24] Tully *et al.*,[25] and Jeong *et al.*[4] were used to derive the 298 K rate coefficient. The temperature dependence was derived from the data of Greiner,[20] Tully *et al.*,[25] and Jeong *et al.*[4]

(j) Derived from the absolute rate coefficient data of Greiner,[20] Overend *et al.*,[21] Howard and Evenson,[22] Leu,[23] Margitan and Watson,[1] Tully *et al.*,[7,25] Jeong *et al.*,[4] Smith *et al.*,[2] and Baulch *et al.*[6] All of these data were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$.

(k) Derived from the rate coefficient data of Greiner,[20,26] Overend *et al.*,[21] Howard and Evenson,[22] Leu,[23] Lee and Tang,[24] Tully *et al.*,[25] Gordon and Mulac,[27] Baldwin and Walker,[28] Baulch *et al.*,[29] and Jeong *et al.*[4] These data were fitted to the Arrhenius expression, $k = A \exp(-B/T)$.

(l) Based directly upon the data and three-parameter equation reported by Tully *et al.*[25]

(m) The 298 K rate coefficient was derived from the data of Greiner,[20] Howard and Evenson,[22] Overend *et al.*,[21] Lee and Tang,[24] Leu,[23] Jeong *et al.*,[4] Tully *et al.*[7,25] and Nielsen *et al.*,[8] using a value of $E/R = 1100$ K to recalculate the room-temperature data to 298 K. The temperature dependence was derived from the data of Greiner,[20] Tully *et al.*,[25] and Jeong *et al.*[4]

Preferred Values

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

$k = 7.4 \times 10^{-12} \exp(-990/T)$ cm^3 molecule^{-1} s^{-1} over the range 230–300 K.

Reliability

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

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

Comments on Preferred Values

The preferred values were obtained by using the absolute rate coefficient data of Greiner,[20] Overend *et al.*,[21] Howard and Evenson,[22] Leu, Margitan and Watson,[1] Tully *et al.*,[7,25] Jeong *et al.*,[4] Smith *et al.*,[23] Baulch *et al.*,[6] Schmidt *et al.*,[5] Devolder *et al.*,[3] Stachnick *et al.*,[9] Wallington *et al.*,[10] Bourmada *et al.*,[11] and Zabarnick *et al.*[12] The data of Gordon and Mulac,[27] Lee and Tang,[24] and Nielsen *et al.*[8] were not included in the evaluation since, while their data are in good agreement with the other rate coefficients[1-7,9-12,20-33,25] for C_2H_6, these studies exhibit significant discrepancies with the consensus literature data for other organic compounds studied. The relative rate coefficients of Baulch *et al.*[29] and Edney *et al.*[13] are in good agreement with the absolute rate coefficient data.

The absolute rate coefficient data used in the evaluation[1-7,9-12,20-33,25] were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.42 \times 10^{-17}$ $T^2 \exp(-461/T)$ cm^3 molecule^{-1} s^{-1} over the range 226–800 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three-parameter equation with $A = C\ e^2\ T^2$, and $B = D + 2T$.

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

$\Delta H_o = -135$ kJ mol^{-1}

Comments

New experiments,[1] generating HO radicals by laser photolysis of flowing N_2O–He–H_2O mixtures and detecting them by LIF, were performed over the pressure range 25 600 Torr in He and over the temperature range 293–480 K. The observed negative temperature coefficients can probably be attributed to falloff effects. Experiments,[2] generating HO by photolysis of H_2O or HNO_3 with LIF detection, at 1 atm of synthetic air and room temperature gave results that, at 295 K, agree well with those from Ref. 1 and our earlier recommendation.[3]

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

$\Delta H^\circ(1) = -81.2$ kJ mol^{-1}
$\Delta H^\circ(2) = -97.0$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute rate coefficients			
$(1.0 \pm 0.2) \times 10^{-12}$	295	Schmidt *et al.*, 1985[1]	(a)
$(1.20 \pm 0.18) \times 10^{-12}$	295	Baulch, Campbell and Saunders, 1985[2]	(b)
$1.04 \times 10^{-16} T^{-12} \exp(-145/T)$	293–854	Droege and Tully, 1986[3]	(c)
$(1.10 \pm 0.04) \times 10^{-12}$	293		
$k_1 = 1.75 \times 10^{-14} T^{0.97} \exp(-798/T)$	293–854	Droege and Tully, 1986[3]	(d)
$k_1 = 3.02 \times 10^{-13}$	298		
$k_2 = 7.76 \times 10^{-17} T^{1.61} \exp(18/T)$	293–854	Droege and Tully, 1986[3]	(d)
$k_2 = 7.94 \times 10^{-13}$	298		
Relative rate coefficients			
2.0×10^{-12}	300	Cox, Derwent and Williams, 1980[4]	(e)
$(1.14 \pm 0.15) \times 10^{-12}$	296	Edney, Kleindienst and Corse, 1986[5]	(f)
Reviews and evaluations			
$1.6 \times 10^{-11} \exp(-800/T)$	290–500	CODATA, 1984[6]	(g)
$1.05 \times 10^{-11} \exp(-590/T)$	300–1000	Warnatz, 1984[7]	(h)
$1.6 \times 10^{-11} \exp(-800/T)$	290–500	NASA, 1985[8]	(i)
$1.27 \times 10^{-17} T^2 \exp(14/T)$	293–854	Atkinson, 1986[9]	(j)
$1.8 \times 10^{-20} T^{2.93} \exp(390/T)$	290–1200	Baulch *et al.*, 1986[10]	(k)
$1.4 \times 10^{-11} \exp(-750/T)$	293–500	NASA, 1987[11]	(l)

Comments

(a) Laser photolysis–laser-induced fluorescence detection of HO in 1 atm of air diluent.

(b) Discharge flow–resonance fluorescence detection of HO.

(c) Laser photolysis–laser-induced fluorescence detection of HO.

(d) These site-specific rate coefficients were derived from the data obtained for C_3H_8, C_3D_8 and a series of partially deuterated propanes.

(e) Relative rate method. HD generated by photolysis of HONO–NO–air mixtures at 1 atm total pressure. Decay of C_3H_8 measured relative to that for C_2H_4 and placed on an absolute basis using $k(HO + C_2H_4) = 8.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[9]

(f) Relative rate method. HO generated by photolysis of CH_3ONO–NO–air mixtures at 1 atm total pressure. Decay of C_3H_8 measured relative to that for n-C_4H_{10}, and placed on an absolute basis using $k(HO + n\text{-}C_4H_{10}) = 2.52 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[9]

(g) The room-temperature rate coefficients of Greiner,[12] Bradley *et al.*,[13] Tully *et al.*,[14] Darnall *et al.*,[15] and Atkinson *et al.*[16] were used to derive the 298 K rate coefficient. The temperature dependence below 500 K was derived from a linear least-squares analysis of the rate coefficients of

Greiner[12] and Tully *et al.*,[14] with the A factor being adjusted to fit the recommended 298 K value.

(h) Utilized the expression of Baldwin *et al.*,[17] based upon the specific rates of attack on the various types of C–H bonds in the molecule.

(i) The room temperature rate coefficients of Greiner,[12] Bradley *et al.*[13] and Tully *et al.*,[14] were used to derive the 298 K rate coefficient. The temperature dependence below 500 K was derived by a linear least-squares analysis of the data of Greiner[12] and Tully *et al.*,[14] with the A factor being adjusted to fit the recommended 298 K value.

(j) Derived from the absolute rate coefficient data of Greiner,[12] Droege and Tully[3] and Baulch *et al.*,[2] and the relative rate coefficient of Atkinson *et al.*[16] (these studies of Droege and Tully[3] and Atkinson *et al.*[16] supersede the previous studies of Tully *et al.*[14] and Darnall *et al.*,[15] respectively). These data[2,3,12,16] were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$. The relative rate coefficient data of Baulch *et al.*[18] are in good agreement with the recommended expression.

(k) The room temperature rate coefficient data of Greiner,[12,19] Darnall *et al.*,[15] Atkinson *et al.*,[16] and Tully *et al.*,[14] were used to derive the 298 K rate coefficient. The temperature dependence was derived from the data of Greiner,[12,19] Gordon and Mulac,[20] Baulch *et al.*,[18] Tully *et al.*,[14] Walker,[21] and Bott and Cohen.[22]

(l) The room temperature rate coefficients of Greiner,[12] Bradley *et al.*,[13] Tully *et al.*,[14] Baulch *et al.*,[18] Schmidt *et al.*,[1] and Droege and Tully[3] were used to derive the 298 K value. The temperature dependence was derived from a least-squares analysis of the rate coefficients of Greiner,[12] Tully *et al.*,[14] and Tully and Droege[3] at < 500 K, with the A factor being adjusted to fit the 298 K value.

Preferred Values

$k = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.6 \times 10^{-12} \exp(-610/T)$ cm^3 molecule^{-1} s^{-1} over a small range around 300 K.

Reliability

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

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

Comments on Preferred Values

The available rate coefficient data exhibit a large amount of scatter, especially at 350 K and below. The absolute rate coefficient data of Greiner,[11] Schmidt *et al.*,[1] Baulch *et al.*,[2] Droege and Tully,[3] and the relative rate coefficient of Atkinson *et al.*[15] (these latter two studies superseding previous studies[14,15] from these groups) were utilized. These data were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.29 \times 10^{-17} T^2 \exp(6/T)$ cm^3 molecule^{-1} s^{-1} over the range 293–854 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K, and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. Note that the data upon which this expression is derived do not extend below 293 K.

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$HO + CO \rightarrow H + CO_2$

$\Delta H^\circ = -104$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute rate coefficients			
$(2.30 \pm 0.16) \times 10^{-13}$ (1 atm N_2)	298	Hofzumahaus and Stuhl, 1984[1]	(a)
$4.05 \times 10^{-14} \exp(667/T) + 3.04 \times 10^9 \exp(-3801/T)$	340–1250	Jonah, Mulac and Zeglinski, 1984[2]	(b)
2.1×10^{-13} (1 atm Ar, 15 Torr H_2O)	298*		
$1.1 \times 10^{-13} \exp(1.08 \times 10^3 T)$	340–1220	Beno, Jonah and Mulac, 1985[3]	(c)
1.5×10^{-13} (1 atm Ar)	298*		
$(1.47 \pm 0.08) \times 10^{-13} (1 + (0.59 \pm 0.10)P/\text{atm})$	262–371	Hynes, Wine and Ravishankara, 1986[4]	(d)
$(1.50 \pm 0.07 \times 10^{-13}(1 + (0.50 \pm 0.07)P/\text{atm})$	237–298	Stachnik and Molina, 1988[5]	(e)
$(2.15 \pm 0.15) \times 10^{-13}$ (1 atm N_2)	298	Wahner and Zetzsch, 1988[6]	(f)
$(2.20 \pm 0.20) \times 10^{-13}$ (1 atm O_2)	298		
$(1.53 \pm 0.15) \times 10^{-13}$ (25 Torr Ar)	298	Brunning *et al.*, 1988[7]	(g)
Reviews and evaluations			
$1.5 \times 10^{-13}(1 + (0.45\ P/\text{atm})$	298	CODATA, 1984[8]	(h)
$1.5 \times 10^{-13} (1 + (0.6\ P/\text{atm})$	298	NASA, 1985[9]	(i)
$1.5 \times 10^{-13} (1 + (0.6\ P/\text{atm})$	200–300	NASA, 1987[10]	(j)

Comments

(a) Flash photolysis—resonance absorption detection of OH.

(b) Pulsed radiolysis Ar/H_2O mixtures—resonance absorption detection of OH in excess CO. Rate constants for HO and DO with CO reported for pressure of 1 atm Ar and 15 Torr H_2O.

(c) As (b) but with OH and varying amount of H_2O.

(d) Pulsed laser photolysis—pulsed laser induced fluorescence. Pressure range 50–700 Torr, O_2 or Air. Expression for $T < 299$ K. No effect of 0.1–20 Torr water vapour.

(e) Pulsed laser photolysis—resonance absorption detection of OH. Up to 730 Torr N_2, O_2 and Air.

(f) Pulsed laser photolysis—long path laser absorption for OH. Pressure = 1 atm N_2 and O_2.

(g) Pulsed photolysis—laser induced fluorescence. Rate coefficients reported for sections of HO ($v = 0,1$) and DO ($v = 0,1$) with CO in 18 or 25 Torr Ar.

(h) Pressure dependent value for 100–760 Torr (air) based on data of Paraskevopoulos and Irwin[11] and DeMore.[12]

(i) Weighted nonlinear least squares fit of pressure dependent data in N_2 and Air from Paraskevopoulos and Irwin[11] and DeMore.[12] Hofzumahaus and Stuhl,[1] Niki *et al.*[9] and unpublished data of Fritz and Zellner and Wine and coworkers. No temperature dependence recommended.

(j) As note (i) but with additional temperature dependence data from Hynes *et al.*,[4] Stachnik and Molina,[5] and Wahner and Zetzsch[6] taken into account.

Preferred Values

$k = 1.5 \times 10^{-13} (1 + 0.6\ P/\text{atm})$ over range 200–300 K and Pressure 0–760 Torr N_2 or Air

Reliability

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

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

Comments on Preferred Values

The experimental results all show excellent agreement on the low pressure (< 100 Torr) value of k and on the pressure dependence of this reaction. The recent investigations of the temperature dependence show that there is little or no temperature dependence under conditions relevant for atmospheric chemistry. At higher temperature, k increases in a strongly nonArrhenius fashion (see review by Tsang and Hampson[14]).

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

$\Delta H^\circ(1) = -135.3$ kJ mol^{-1}
$\Delta H^\circ(2) = -91.5$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute rate coefficients			
$(8.1 \pm 0.5) \times 10^{-12}$	296	Temps and Wagner, 1984[1]	(a)
$(1.66 \pm 0.20) \times 10^{-11} \exp[(-86 \pm 40)/T]$	296–576	Zabarnick, Fleming and Lin, 1988[2]	(b)
$(1.25 \pm 0.11) \times 10^{-11}$	298		
Relative rate coefficients			
$(8.4 \pm 0.5) \times 10^{-12}$	299	Niki *et al.*, 1984[3]	(c)
Branching ratios			
$k_1/k = 1.00 \pm 0.05$	296	Temps and Wagner, 1984[1]	(a)
$k_2/k < 0.02$	299	Niki *et al.*, 1984[3]	(c)
Reviews and evaluations			
1.1×10^{-11}	200–425	CODATA, 1984[4]	(d)
$5.0 \times 10^{-11} \exp(-600/T)$	300–2500	Warnatz, 1984[5]	(e)
1.0×10^{-11}	228–426	NASA, 1985[6]	(f)
9.0×10^{-12}	228–426	Atkinson, 1986[7]	(g)
$5.7 \times 10^{-15} T^{1.18} \exp(225/T)$	300–1600	Tsang and Hampson, 1986[8]	(h)
1.0×10^{-11}	228–426	NASA, 1987[9]	(f)

Comments

(a) Discharge flow–laser magnetic resonance detection of HO and HCO. Rate coefficient ratio k_1/k obtained from the amount of HCO formed compared to HO consumed.

(b) Laser photolysis–laser-induced fluorescence detection of HO.

(c) Relative rate method. HO radicals generated by photolysis of CH_3ONO–NO–air and C_2H_5ONO–NO–air mixtures at 700 Torr total pressure of air. Decay rates of $HC^{13}HO$ and C_2H_4 monitored by infrared spectroscopy. Relative rate constant ratio of $k/k(HO + C_2H_4) = 0.99 \pm 0.06$ placed on an absolute basis by use of $k(HO + C_2H_4) = 8.50 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[7] Assumed that the C^{13} isotope effect is negligible. The ratio $k_2/k < 0.02$ was determined from the lack of observation of $HC^{13}OOH$ as a product.

(d) Derived from the mean of the rate coefficients determined by Morris and Niki,[10] Atkinson and Pitts,[11] and Stief *et al.*[12]

(e) Based mainly on the rate coefficient data of Atkinson and Pitts,[11] Peeters and Mahnen,[13] and Vandooren and van Tiggelen.[14]

(f) The 298 K rate coefficient was the mean of the absolute rate coefficients determined by Atkinson and Pitts[11] and Stief *et al.*[12] These data[11,12] yield no evidence for any temperature dependence of the rate coefficient.

(g) Derived from the rate coefficient data of Atkinson and Pitts,[9] Stief *et al.*,[12] Temps and Wagner[1] and Niki *et al.*,[3] with the assumption of no temperature dependence based upon the data of Atkinson and Pitts[11] and Stief *et al.*[12]

(h) Based upon the rate coefficient data of Atkinson and Pitts,[11] Stief *et al.*,[12] Peeters and Mahnen,[13] and Vandooren and van Tiggelen.[14]

Preferred Values

$k = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.6 \times 10^{-11} \exp(-110/T)$ cm^3 molecule^{-1} s^{-1} over the range 230–580 K.

$k_1/k = 1.0$ at 298 K.

Reliability

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

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

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

Comments on Preferred Values

The preferred values are derived from a least-squares analysis of the absolute rate coefficients determined by Atkinson and Pitts,[11] Stief *et al.*,[12] Temps and Wagner,[1] and Zabarnick *et al.*,[2] which are in reasonably good agreement at room temperature. The relative rate coefficients of Morris and Niki,[10] and Niki *et al.*,[3,15] are consistent with the preferred 298 K value.

The product data of Temps and Wagner[1] and Niki *et al.*[3] show that at 298 K this reaction proceeds essentially totally via pathway (1) to yield $H_2O + HCO$.

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$HO + CH_3CHO \rightarrow H_2O + CH_3CO$

$\Delta H^\circ = -139.6$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute rate coefficients			
$(7.1 \pm 0.2) \times 10^{-12} \exp[(165 \pm 91)/T]$	253–424	Semmes *et al.*, 1985[1]	(a)
$(1.22 \pm 0.27) \times 10^{-11}$	298		
$(5.52 \pm 0.80) \times 10^{-12} \exp[(307 \pm 52)/T]$	244–528	Michael, Keil and Klemm, 1985[2]	(b)
$(1.47 \pm 0.28) \times 10^{-11}$	298		
Reviews and evaluations			
$6.9 \times 10^{-12} \exp(260/T)$	298–450	CODATA, 1984[3]	(c)
1.7×10^{-11}	300–2000	Warnatz, 1984[4]	(d)
$6.87 \times 10^{-12} \exp(256/T)$	299–426	Atkinson, 1986[5]	(e)
$6.0 \times 10^{-12} \exp(250/T)$	244–528	NASA, 1987[6]	(f)

Comments

(a) Flash photolysis–resonance fluorescence detection of HO. Difficulties were encountered with determining the acetaldehyde concentrations.

(b) Discharge flow–resonance fluorescence detection of HO.

(c) Based on the absolute rate coefficient study of Atkinson and Pitts.[7] Other available absolute[8] and relative[9–11] rate coefficient data are in good agreement with this rate coefficient.

(d) Based on the room-temperature data of Atkinson and Pitts,[7] Morris *et al.*,[8] Cox *et al.*,[9] and Niki *et al.*,[10] with an assumed zero temperature dependence.

(e) Based on the absolute rate coefficient study of Atkinson and Pitts,[7] which is in excellent agreement with the relative rate coefficient measured by Niki *et al.*[10] at 298 K. The data of Semmes *et al.*[1] were not used in the evaluation because of their reported difficulties in determining the acetaldehyde concentration.

(f) The 298 K rate coefficient was based upon the rate coefficient data of Morris *et al.*,[8] Niki *et al.*,[10] Atkinson and Pitts,[7] Kerr and Sheppard,[11] Semmes *et al.*,[1] and Michael *et al.*[2] The temperature dependence was the average of those measured by Atkinson and Pitts,[7] Semmes *et al.*,[1] and Michael *et al.*[2]

Preferred Values

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

$k = 5.6 \times 10^{-12} \exp(310/T)$ cm^3 molecule^{-1} s^{-1} over the range 240–530 K.

Reliability

$\Delta \log k = \pm 0.1$ 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[7] and Michael *et al.*,[2] and the relative rate coefficient of Niki *et al.*[10] at 298 K. The absolute and relative rate data of Morris *et al.*,[8] Cox *et al.*,[9] and Kerr and Sheppard[11] are in agreement with the preferred 298 K value. The data of Semmes *et al.*,[1] 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.

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$HO + C_2H_5CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute rate coefficients			
$(1.71 \pm 0.24) \times 10^{-11}$	298	Semmes *et al.*, 1985[1]	(a)
Relative Rate Coefficients			
3.06×10^{-11}	298	Morris and Niki, 1971[2]	(b)
$(2.22 \pm 0.09) \times 10^{-11}$	298	Niki *et al.*, 1978[3]	(c)
$(1.95 \pm 0.15) \times 10^{-11}$	298	Kerr and Sheppard, 1981[4]	(c)
$(1.83 \pm 0.21) \times 10^{-11}$	298	Audley, Baulch and Campbell, 1981[5]	(d)
$< 2.8 \times 10^{-11}$	296	Kerr and Stocker, 1985[6]	(e)
Reviews and Evaluations			
1.96×10^{-11}	298	Atkinson, 1986[7]	(f)

Comments

(a) Flash photolysis–resonance fluorescence detection of HO.

(b) Discharge flow–mass spectrometric detection of 1-propanal and propene in the presence of excess HO radicals. Rate coefficient determined relative to that for propene, and placed on an absolute basis using $k(HO + \text{propene}) = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} under the experimental conditions used.[8]

(c) Relative rate method. HO radicals generated by photolysis of HONO in air at atmospheric pressure. Decay of 1-propanal monitored relative to that for ethene, and placed on an absolute basis using $k(HO + \text{ethene}) = 8.54 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[7]

(d) Relative rate method. HO radicals generated from the heterogeneous reaction of H_2O_2 with NO_2. Rate coefficient measured relative to that for acetaldehyde, and placed on an absolute basis by use of $k(HO + CH_3CHO) = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(e) Relative rate method. Rate coefficient determined relative to that for HO + HONO from the observed dependence of the rate of change of NO on the NO_x/C_2H_5CHO concentration ratio, and placed on an absolute basis by use of $k(HO + HONO) = 4.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(f) Derived from the absolute rate coefficient of Semmes *et al.*[1] and the relative rate coefficients of Niki *et al.*[3] and Kerr and Sheppard.[4]

Preferred Values

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

Reliability of Preferred Values

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

Comments on Preferred Values

Derived from the mean of the absolute rate coefficient of Semmes *et al.*[1] and the relative rate coefficients of Niki *et al.*[3] and Kerr and Sheppard.[4] 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.*[5] was not used in the evaluation, due to questions concerning the applicability of the experimental technique used.[1,7] The rate coefficient derived by Kaiser[9] at 553 K relative to those for ethene, propene and *trans*-2-butene of $\lesssim 2.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, though of only semi-quantitative 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[7] to be H-atom abstraction from the –CHO group to form $H_2O + C_2H_5CO$.

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

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative rate coefficients			
$(1.12 \pm 0.04) \times 10^{-11}$	298	Plum *et al.*, 1983[1]	(a)

Comments

(a) Relative rate method. HO radicals generated by photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. Relative decay rates of glyoxal and cyclohexane monitored in the presence of varying concentrations of HO radicals. Relative rate coefficient placed on an absolute basis by use of $k(HO + cyclohexane) = 7.38 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[2]

Preferred Values

$k = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

Based on the sole study of Plum *et al.*,[1] with the uncertainty limits increased to reflect this. 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 $H_2O + HC(O)CO$.

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$$\begin{aligned} HO + HOCH_2CHO &\rightarrow H_2O + HOCH_2CO \quad (1) \\ &\rightarrow H_2O + HOCHCHO \quad (2) \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative rate coefficients			
$(1.0 \pm 0.1) \times 10^{-11}$	298	Niki *et al.*, 1987[1]	(a)
Branching ratios			
$k_2/k = 0.20$ $k_1/k = 0.80$	298	Niki *et al.*, 1987[1]	(a)

Comments

(a) HO radicals generated by photolysis of CH_3OHO–NO–air and C_2H_5ONO–NO–air mixtures at 700 Torr total pressure. Rate coefficient measured relative to that for reaction of HO radicals with CH_3CHO, and placed on an absolute basis by use of $k(HO + CH_3CHO) = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Branching ratio determined by measuring the formation of the $(CHO)_2$, CO_2 and HCHO products, with $(CHO)_2$ being produced by reaction of O_2 with the HOCHCHO radical formed in step (2), and CO_2 + HCHO being produced from the $HOCH_2CO$ radical formed in step (1).

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.

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

Comments on Preferred Values

Taken from the recent study of Niki *et al.*,[1] with the error limits increased accordingly.

References

[1] H. Niki, P. D. Maker, C. M. Savage, and M. D. Hurley, J. Phys. Chem. **91**, 2174 (1987).

$HO + CH_3COCHO \rightarrow H_2O + CH_3COCO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute rate coefficients			
$(7.1 \pm 1.6) \times 10^{-12}$	297	Kleindienst, Harris and Pitts, 1982[1]	(a)
Relative rate coefficients			
$(1.69 \pm 0.12) \times 10^{-11}$	298	Plum *et al.*, 1983[2]	(b)

Comments

(a) Flash photolysis–resonance fluorescence detection of HO.

(b) Relative rate method. HO radicals generated by photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. Relative decay rates of methylglyoxal and cyclohexane monitored in the presence of varying concentrations of HO radicals. Relative rate coefficients placed on an absolute basis by use of k(HO + cyclohexane) = 7.38×10^{-12} cm^3 molecule^{-1} s^{-1}.[3]

Preferred Values

$k = 1.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

Based upon the data obtained by Plum *et al.*[2] The absolute rate coefficient measured by Kleindienst, Harris and Pitts[1] may have been low due to the presence of significant levels of low reactivity impurities in the methylglyoxal. A close to zero temperature dependence is expected at around room temperature. The reaction is assumed to proceed via H-atom abstraction to form $H_2O + CH_3COCO$.

References

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

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

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$HO + CH_3COCH_3 \rightarrow H_2O + CH_3COCH_2$

$\Delta H° = -87.8$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute rate coefficients			
$(1.7\pm0.4)\times10^{-12}\exp[-(600\pm75)/T]$	240–440	Wallington and Kurylo, 1987[1]	(a)
$(2.16\pm0.16)\times10^{-13}$	296		
Relative rate coefficients			
$\leqslant5\times10^{-13}$	300	Cox, Derwent and Williams, 1980[2]	(b)
$(6.2\pm0.9)\times10^{-13}$	298	Chiorboli *et al.*, 1983[3]	(c)
$(2.7\pm0.8)\times10^{-13}$	303	Kerr and Stocker, 1986[4]	(d)

Comments

(a) Flash photolysis–resonance fluorescence detection of HO.

(b) Relative rate method. HO radicals generated by photolysis of HONO–air mixtures at atmospheric pressure. Relative decay rate of CH_3COCH_3 measured relative to those for ethene and toluene. Due to photolysis of CH_3COCH_3, the measured decay rate is an upper limit to that due to HO radical reaction.

(c) Relative rate method. HO radicals generated by photolysis of organic–NO–air mixtures at atmospheric pressure in a chamber. Relative decay rates of CH_3COCH_3 and n-hexane measured, placed on an absolute basis by use of k(HO + n-hexane) $-$ 5.58×10^{-12} cm^3 molecule^{-1} s^{-1}.[5]

(d) Relative rate method. HO radicals generated by photolysis of HONO–air mixtures at atmospheric pressure in a chamber. Decay rate of CH_3COCH_3 measured relative to that for ethene, with account being taken of the concurrent photolysis of CH_3COCH_3. Placed on an absolute basis by use of $k(HO + C_2H_4) = 8.35\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[5]

Preferred Values

$k = 2.3\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.7\times10^{-12}\exp(-600/T)$ cm^3 molecule^{-1} s^{-1} over the range 240–440 K.

Reliability

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

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

Comments on Preferred Values

Based on the absolute study of Wallington and Kurylo,[1] which is in good agreement with the relative rate coefficient of Kerr and Stocker[4] and consistent with that of Cox *et al.*[2] The higher rate coefficient reported by Chiorboli *et al.*[3] could be due to photolysis of CH_3COCH_3, which was not taken into account.

References

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

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

[3] C. Chiorboli, C. A. Bignozzi, A. Maldotti, P. F. Giardini, A. Rossi, and V. Carassiti, Int. J. Chem. Kinet. **15**, 579 (1983).

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

[5] R. Atkinson, Chem. Rev. **88**, 69 (1986).

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

$\Delta H^\circ(1) = -105.4$ kJ mol^{-1}
$\Delta H^\circ(2) = -61.9$ 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			
$(1.2 \pm 0.3) \times 10^{-11} \exp[-(810 \pm 50)/T]$	295–420	Hägele *et al.*, 1983[1]	(a)
$(7.8 \pm 1.5) \times 10^{-13}$	295		
$(1.1 \pm 0.3) \times 10^{-11} \exp[-(798 \pm 45)/T]$	300–1020	Meier,$_2$Grotheer and Just, 1984[2]	(b)
7.7×10^{-13}	300		
$(8.0 \pm 1.9) \times 10^{-12} \exp[-(664 \pm 88)/T]$	260–803	Greenhill and O'Grady, 1986[3]	(c)
$(7.5 \pm 0.8) \times 10^{-13}$	300		
$(4.8 \pm 1.2) \times 10^{-12} \exp[-(480 \pm 70)/T]$	240–440	Wallington and Kurylo, 1987[4]	(d)
$(8.61 \pm 0.47) \times 10^{-13}$	296		
Relative rate coefficients			
1.10×10^{-12}	300	Barnes *et al.*, 1982[5]	(e)
$(9.45 \pm 0.72) \times 10^{-13}$	300	Tuazon *et al.*, 1983[6]	(f)
1.2×10^{-12}	300	Klöpffer *et al.*, 1986,[7] 1988[8]	(g)
Branching ratios			
$k_2/k = 0.11 \pm 0.03$	298	Hägele *et al.*, 1983[1]	(h)
$= 0.22 \pm 0.07$	393		
$k_2/k = 0.25 \pm 0.08$	~300	Meier *et al.*, 1984[2]	(i)
$= 0.17 \pm 0.13$			
Reviews and Evaluations			
1.0×10^{-12}	298	CODATA, 1984[9]	(j)
$1.34 \times 10^{-11} \exp(-805/T)$	298–420	Atkinson, 1986[10]	(k)

Comments

(a) Laser photolysis–resonance fluorescence detection of HO.

(b) Discharge flow–laser induced fluorescence detection of HO.

(c) Flash photolysis–resonance absorption detection of HO.

(d) Flash photolysis–resonance fluorescence detection of HO.

(e) Relative rate method. HO radicals generated from the thermal decomposition of HO_2NO_2 in the presence of NO at atmospheric pressure. Relative decay rates of CH_3OH and C_2H_4 measured, and placed on an absolute basis by use of $k(HO + C_2H_4) = 8.45 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[10]

(f) Relative rate method. HO radicals generated from the dark reaction of N_2H_4 with O_3. Relative decay rates of CH_3OH and CH_3OCH_3 measured, and placed on an absolute basis by use of $k(HO + CH_3OCH_3) = 3.01 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[10]

(g) Relative rate method. HO radicals generated from the photolysis of HONO–air and NO_x–organic–air mixtures. Relative decay rates of CH_3OH and an unspecified reference organic monitored. No details given.

(h) Laser photolysis–laser induced fluorescence detection of CH_3O formed from the reaction of HG radicals with CH_3OH, using HNO_3 as a source of HO radicals and calibrating the CH_3O signal by photodissociation of CH_3ONO.

(i) CH_3O radicals detected by laser-induced fluorescence, using the $F + CH_3OH$ reaction to calibrate the system. Branching ratio was also determined less accurately by mass-spectrometric detection of CH_2OH radicals.

(j) Based on the absolute rate coefficients of Overend and Paraskevopoulos[11] and Ravishankara and Davis.[12]

(k) The 298 K rate coefficient based on the absolute and relative rate coefficient data of Overend and Paraskevopoulos,[11] Ravishankara and Davis,[12] Barnes *et al.*[5] Tuazon *et al.*,[6] Hägele *et al.*,[1] Meier *et al.*[2] and Zetzsch (unpublished data, 1982). The temperature dependence was taken from the data of Hägele *et al.*[1] and Meier *et al.*[2]

Preferred Values

$k = 9.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.1 \times 10^{-12} \exp(-690/T)$ cm^3 molecule^{-1} s^{-1} over the range 240–1000 K.

Reliability

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

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

Comments on Preferred Values

The 298 K rate coefficient is based upon the room-temperature absolute rate coefficients of Overend and Paraskevopoulos,[11] Ravishankara and Davis,[12] Hägele *et al.*,[1] Meier *et al.*,[2] Greenhill and O'Grady,[3] and Wallington and Kurylo[4] and the relative rate coefficients of Barnes *et al.*[5] and Tuazon *et al.*[6] The temperature dependence is the average of those reported from the absolute rate coefficient studies,[1–4] with the A factor being adjusted to yield the 298 K value. The product studies[1,2] show that the reaction proceeds mainly by step (1) at room temperature, as expected from the thermochemistry of the reaction steps (1) and (2).

References

[1]J. Hagele K. Lorenz D. Rhasa and R. Zellner, Ber. Bunsenges Phys. Chem. **87**, 1023 (1983).
[2]U. Meier, H. H. Grotheer, and Th. Just, Chem. Phys. Lett. **106**, 97 (1984).
[3]P. G. Greenhill and B. V. O'Grady, Aust. J. Chem. **39**, 1775 (1986).
[4]T. J. Wallington and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 1015 (1987).
[5]I. Barnes, V. Bastian, K. H. Becker, E. H. Fink, and F. Zabel, Atmos. Environ. **16**, 545 (1982).
[6]E. C. Tuazon, W. P. L. Carter, R. Atkinson, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **15**, 619 (1983).
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[8]W. Klöpffer, F. Haag, E.-G. Kohl, and R. Frank, Ecotoxicol. Environ. Safety **15**, 298 (1988).
[9]CODATA, Supplement II, 1984 (see references in the Introduction).
[10]R. Atkinson, Chem. Rev. **86**, 69 (1986).
[11]R. Overend and G. Paraskevopoulos, J. Phys. Chem. **82**, 1329 (1978).
[12]A. R. Ravishankara and D. D. Davis, J. Phys. Chem. **82**, 2852 (1978).

$HO + C_2H_5OH \rightarrow H_2O + CH_2CH_2OH$ (1)
$\rightarrow H_2O + CH_3CHOH$ (2)
$\rightarrow H_2O + CH_3CH_2O$ (3)

$\Delta H^\circ(3) = -63.5$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute rate coefficients			
$(3.74 \pm 0.37)\times10^{-12}$	296	Overend and Paraskevopoulos, 1978[1]	(a)
$(2.62 \pm 0.36)\times10^{-12}$	298	Ravishankara and Davis, 1978[2]	(b)
$(1.25 \pm 0.24)\times10^{-11}\exp[-(360 \pm 52)/T]$	255–459	Greenhill and O'Grady, 1986[3]	(a)
$(3.40 \pm 0.17)\times10^{-12}$	293		
$(5.16 \pm 1)\times10^{-12}\exp[-(274 \pm 90)/T]$	300–1000	Meier *et al.*, 1987[4]	(c)
2.07×10^{-12}	300		
$(7.4 \pm 3.2)\times10^{-12}\exp[-(240 \pm 110)/T]$	240–440	Wallington and Kurylo, 1987[5]	(b)
$(3.33 \pm 0.23)\times10^{-12}$	296		
Relative rate coefficients			
$(3.25 \pm 0.51)\times10^{-12}$	292	Campbell *et al.*, 1976[6]	(d)
$(3.7 \pm 0.6)\times10^{-12}$	303	Kerr and Stocker, 1986[7]	(e)
Branching ratios			
$k_2/k = 0.75 \pm 0.15$	300	Meier *et al.*, 1985[8]	(f)
Reviews and evaluations			
$5.27\times10^{-12}\exp-(176/T)$	296–609	Atkinson, 1986[9]	(g)

Comments

(a) Flash photolysis–resonance absorption detection of HO.

(b) Flash photolysis–resonance fluorescence detection of HO.

(c) Discharge flow–laser induced fluorescence detection of HO. The Arrhenius expression given in the table supersedes that given in the earlier publication of Meier *et al.*,[8] with corrections being made for the existence of nonlinear temperature gradients in the flow reactor.[4]

(d) Relative rate method. HO radicals generated from the heterogeneous reaction of H_2O_2 with NO_2. Rate coefficient derived relative to that for *n*-butane, and placed on an absolute basis by use of $k(HO + n\text{-butane}) = 2.44\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[9]

(e) Relative rate method. HO radicals generated from the photolysis of HONO–air mixtures at atmospheric pressure. Relative decay rates of ethanol and ethene measured, and the relative rate coefficient ratio placed on an absolute basis by use of $k(HO + \text{ethene}) = 8.35\times10^{12}$ cm^3 molecule^{-1} s^{-1}.[9]

(f) Derived from a discharge flow–mass-spectrometric study of the products formed from this reaction.

(g) Derived from the absolute rate coefficient data of Overend and Paraskevopoulos,[1] Ravishankara and Davis,[2] and Lorenz, Rhäsa, and Zellner (unpublished data, 1984).

Preferred Values

$k = 3.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.3\times10^{-12}\exp(-300/T)$ cm^3 molecule^{-1} s^{-1} over the range 250–450 K.

Reliability

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

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

Comments on Preferred Values

There is a substantial scatter in the room-temperature rate coefficients measured to date. The data of Meier *et al.*[4] are substantially lower than the other rate coefficient data, and have not been used in the derivation of the preferred values. The 298 K rate coefficient is the average of the room-temperature absolute and relative rate coefficient data of Overend and Paraskevopoulos,[1] Ravishankara and Davis,[2] Greenhill and O'Grady,[3] Wallington and Kurylo,[5] and Kerr and Stocker.[7]

The temperature dependence is the mean of those reported by Greenhill and O'Grady[3] and Wallington and Kurylo[5] (and is similar to that determined by Meier *et al.*[4]). The study of Meier *et al.*[8] determined that at room temperature the reaction proceeds mainly via formation of the CH_3CHOH radical, consistent with the expected thermochemistry of the reaction steps.

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).
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[9] R. Atkinson, Chem. Rev. **86**, 69 (1986).

$HO + n\text{-}C_3H_7OH \rightarrow$ Products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute rate coefficients			
$(5.33 \pm 0.53) \times 10^{-12}$	296	Overend and Paraskevopoulos, 1978[1]	(a)
$(5.34 \pm 0.29) \times 10^{-12}$	296	Wallington and Kurylo, 1987[2]	(b)
Relative rate coefficients			
$(4.07 \pm 0.65) \times 10^{-12}$	292	Campbell, McLaughlin, and Handy, 1976[3]	(c)

Comments

(a) Flash photolysis–resonance absorption detection of HO.

(b) Flash photolysis–resonance fluorescence detection of HO.

(c) Relative rate method. HO radicals generated from the dark heterogeneous reaction of H_2O_2 with NO_2. Rate coefficient measured relative to that for *n*-butane, placed on an absolute basis by use of $k(HO + n\text{-butane}) = 2.44 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[4]

Preferred Values

$k = 5.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The experimental technique of Campbell *et al.*,[3] is possibly prone to unrecognized problems,[4] 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] and Wallington and Kurylo.[2]

References

[1] R. Overend and G. Paraskevopoulos, J. Phys. Chem. **82**, 1329 (1976).
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[3] I. M. Campbell, D. F. McLaughlin, and B. J. Handy, Chem. Phys. Lett. **38**, 362 (1976).
[4] R. Atkinson, Chem. Rev. **88**, 69 (1986).

$HO + i\text{-}C_3H_7OH \rightarrow$ Products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute rate coefficients			
$(5.48 \pm 0.55) \times 10^{-12}$	296	Overend and Paraskevopoulos, 1978[1]	(a)
$(5.8 \pm 1.9) \times 10^{-12} \exp[-(30 \pm 90)/T]$	240–440	Wallington and Kurylo, 1987[2]	(b)
$(5.81 \pm 0.34) \times 10^{-12}$	296		
Relative Rate Coefficients			
$(6.9 \pm 2.1) \times 10^{-12}$	305	Lloyd *et al.*, 1976[3]	(c)
5.1×10^{-12}	300	Klöpffer *et al.*, 1986,[4] 1988[5]	(d)

Comments

(a) Flash photolysis–resonance absorption detection of HO.

(b) Flash photolysis–resonance fluorescence detection of HO.

(c) Relative rate method. HO radicals generated by photolysis of NO–NO_2–organic–air mixtures at atmospheric pressure. Decay rate of 2-propanol measured relative to that for 2-methylpropene. Dilution of the reactant mixtures during the irradiations had to be taken into account. The rate coefficient ratio measured was placed on an absolute basis by use of $k(HO + \text{2-methylpropene}) = 4.95\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[6]

(c) Relative rate method. HO radicals generated by photolysis of HONO–air mixtures at atmospheric pressure. Relative decay rates of 2-propanol and an unspecified reference organic monitored. No details given.

Preferred Values

$k = 5.6\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K, independent of temperature over the range 240–440 K.

Reliability

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

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

Comments on Preferred Values

The preferred rate coefficient at 298 K is the average of those of Overend and Paraskevopoulos[1] and Wallington and Kurylo,[2] and is in agreement with the relative rate coefficients reported by Lloyd *et al.*[3] and Klöpffer *et al.*[4,5] A zero temperature dependence is used, in agreement with the data of Wallington and Kurylo.[2]

References

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[6] R. Atkinson, Chem. Rev. **86**, 69 (1986).

$HO + CH_3OOH \rightarrow H_2O + CH_2OOH$ (1)
$\rightarrow H_2O + CH_3OO$ (2)

$\Delta H^\circ(2) = -127.1$ kJ mol^{-1}

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

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Relative rate coefficients			
$(1.06 \pm 0.1)\times10^{-11}$	~298	Niki *et al.*, 1983[1]	(a)
Branching ratio			
$k_1/k = 0.44 \pm 0.10$	~298	Niki *et al.*, 1983[1]	(a)
Reviews and evaluations			
1.0×10^{-11}	298	NASA, 1985[2]	(b)
1.0×10^{-11}	298	NASA, 1987[3]	(b)

Comments

(a) HO radicals generated by photolysis of CH_3ONO–NO–air and C_2H_5ONO–NO–air mixtures at 700 Torr total pressure. Rate coefficients k determined relative to those for the HO radical reactions with ethene and acetaldehyde. Using rate coefficients of $k(HO + C_2H_4) = 8.54\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} [4] and $k(HO + CH_3CHO) = 1.6\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, rate coefficients k of $(1.02 \pm 0.08)\times10^{-11}$ and $(1.09 \pm 0.11)\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, respectively, are obtained. The value given in the table is the mean of these. The branching ratio was determined from a product study.

(b) Based upon the data of Niki *et al.*[1]

Preferred Values

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

$k_1/k = 0.4$ at 298 K.

Reliability

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

$\Delta(k_1/k) = 0.2$ at 298 K.

Comments on Preferred Values

The preferred values are those of Niki *et al.*[1] with increased error limits. A close to zero temperature dependence is expected at around room temperature.[2,3]

References

[1] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **87**, 2190 (1983).

[2] NASA Evaluation No. 7, 1985 (See References in Introduction).

[3] NASA Evaluation No. 8, 1987 (See References in Introduction).

[4] R. Atkinson Chem. Rev. **86**, 69 (1986).

$HO + HCOOH \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.62 \pm 0.78) \times 10^{-13}$	298–430	Wine, Astalos, and Mauldin, 1985	(a)
$(4.90 \pm 0.12) \times 10^{-13}$	296	Jolly *et al.*, 1986[2]	(b)
$(3.7 \pm 0.4) \times 10^{-13}$	298	Dagaut *et al.*, 1988[3]	(a)

Comments

(a) Flash photolysis–resonance fluorescence detection of HO.

(b) Laser photolysis–resonance absorption detection of HO.

Preferred Values

$k = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–430 K.

Reliability

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

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

Comments on Preferred Values

A major problem with the determination of the rate coefficient for this reaction concerns the ready dimerization of HCOOH. The studies of Wine *et al.*[1] and Jolly *et al.*[2] monitored formic acid in the experimental systems used by ultraviolet absorption spectroscopy. The data from these two studies[1,2] agree well, and are in reasonable agreement with the rate coefficient of Dagaut *et al.*[3] The mean of the room temperature data of Wine *et al.*[1] and Jolly *et al.*[2] has been used to derive the preferred 298 K value. The temperature dependence of the rate coefficient has been taken to be zero, in agreement with the data of Wine *et al.*[1]

Recent 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] This reaction is presumed to proceed mainly by

$$\begin{tikzcd} \mathrm{OH} + \mathrm{HCOOH} \arrow[r] & \mathrm{H_2O} + \mathrm{COOH} \arrow[d] \\ & \mathrm{H} + \mathrm{CO_2} \end{tikzcd}$$

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

$HO + CH_3COOH \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.3 \pm 0.1) \times 10^{-12} \exp[-(170 \pm 20)/T]$	298–440	Dagaut *et al.*, 1988[1]	(a)
$(7.4 \pm 0.6) \times 10^{-13}$	298		

Comments

(a) Flash photolysis–resonance fluorescence detection of HO.

Preferred Values

$k = 7.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3 \times 10^{-12} \exp(-170/T)$ cm^3 molecule^{-1} s^{-1} over the range 290–440 K.

Reliability

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

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

Comments on Preferred Value

The preferred values are based upon the sole study.[1]

References

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

$HO + CH_3CO_3NO_2 \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$< 1.7 \times 10^{-13}$	299	Winer *et al.*, 1977[1]	(a)
$1.23 \times 10^{-12} \exp[-(651 \pm 229)/T]$	273–297	Wallington, Atkinson, and Winer, 1984[2]	(a)
$(1.37 \pm 0.05) \times 10^{-13}$	297		

Comments

(a) Flash photolysis-resonance fluorescence detection of HO.

Preferred Values

$k = 1.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.2 \times 10^{-12} \exp(-650/T)$ cm^3 molecule^{-1} s^{-1} over the range 270–300 K.

Reliability

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

$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

Based upon the absolute rate coefficient study of Wallington *et al.*,[2] which is consistent with the upper limit to the rate coefficient previously determined by Winer *et al.*[1] using a similar experimental technique. The reaction is expected to proceed via H-atom abstraction from the C–H bonds to yield $H_2O + CH_2CO_3NO_2$.

References

[1] 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).

$HO + HCN \rightarrow$ Products

Comments

The study of Fritz *et al.*,[1] which was discussed in the previous CODATA evaluation[2] and was the basis for the preferred values, has been published.

References

[1] B. Fritz, K. Lorenz, W. Steinert, and R. Zellner, Oxid. Commun. **6**, 363 (1984).

[2] CODATA, Supplement II, 1984 (See References in Introduction).

$HO + CH_3CN \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.3) \times 10^{-14}$	295	Poulet *et al.*, 1984[1]	(a)
Relative Rate Coefficients			
$< 1.0 \times 10^{-13}$	300	Klöpffer *et al.*, 1986,[2] 1988[3]	(b)
Reviews and Evaluations			
$6.7 \times 10^{-13} \exp(-890/T)$	250–420	CODATA, 1984[4]	(c)
$4.5 \times 10^{-13} \exp(-900/T)$	250–391	NASA, 1985[5]	(d)
$6.78 \times 10^{-13} \exp(-1040/T)$	250–363	Atkinson, 1986[6]	(e)
$4.5 \times 10^{-13} \exp(-900/T)$	250–391	NASA, 1987[7]	(d)

Comments

(a) Discharge flow–electron paramagnetic resonance detection of HO.

(b) Relative rate method. HO radicals generated by photolysis, at wavelengths $\gtrsim 300$ nm, of HONO–air mixtures at 1 atm total pressure. Relative decay rates measured. No details given concerning the reference organic used.

(c) Derived from the absolute rate coefficient data of Harris *et al.*[8] and Kurylo and Knable.[9]

(d) The 298 K value was derived from the average of the absolute rate coefficients of Kurylo and Knable,[9] Zetzsch (unpublished data, 1983), Rhasa and Zellner (unpublished data, 1984) and Poulet *et al.*[1] The temperature dependence was obtained from the data of Rhasa and Zellner (unpublished data, 1984) and Kurylo and Knable.[9]

(e) Derived from a least-squares analysis of the data of Fritz *et al.*,[10] Poulet *et al.*,[1] Zetzsch (unpublished data, 1983), and Kurylo and Knable.[9]

Preferred Values

$k = 2.0\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.3\times10^{-13}\exp(-1030/T)$ cm^3 molecule^{-1} s^{-1} over the range 250–360.

Reliability

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

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

Comments on Preferred Values

The absolute room-temperature rate coefficients reported by Kurylo and Knable[9] and Poulet *et al.*[1] are in good agreement and imply a lack of a pressure dependence on the rate coefficient for this reaction over the total pressure range ~1–50 Torr. The earlier data of Harris *et al.*[8] are higher by a factor of ~2, and are neglected.

The preferred 298 K value is the average of the rate coefficients reported by Kurylo and Knable[9] and Poulet *et al.*[1] The temperature dependence is that of Kurylo and Knable,[9] with the *A* factor being adjusted to fit the preferred 298 K value.

References

[1] G. Poulet, G. Laverdet, J. L. Jourdain, and G. LeBras, J. Phys. Chem. **88**, 6259 (1984).
[2] W. Klöpffer, R. Frank, E.-G. Kohl, and F. Haag, Chemiker-Zeitung **110**, 57 (1986).
[3] W. Klöpffer, F. Haag, E.-G. Kohl, and R. Frank, Ecotoxicol. Environ. Safety **15**, 298 (1988).
[4] CODATA, Supplement II, 1984 (See References in Introduction).
[5] NASA Evaluation No. 7, 1985 (See References in Introduction).
[6] R. Atkinson, Chem. Rev. **86**, 69 (1986).
[7] NASA Evaluation No. 8, 1987 (See References in Introduction).
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[9] M. J. Kurylo and G. L. Knable, J. Phys. Chem. **88**, 3305 (1984).
[10] B. Fritz, K. Lorenz, W. Steinert, and R. Zellner, in *Proceedings of the 2nd European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants* (Riedel, Boston, 1982), pp. 192–202.

$HO_2 + CH_3O_2 \rightarrow O_2 + CH_3O_2H$

$\Delta H^\circ = -169$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.4\pm1.0)\times10^{-12}$	298	McAdam, Veyret, and Lesclaux, 1987[1]	(a)
$(2.9\pm0.4)\times10^{-12}$	298	Kurylo *et al.*, 1987[2]	(b)
$(3.0\pm1.2)\times10^{-13}\exp(720\pm100/T)$	228–380	Dagaut, Wallington, and Kurylo, 1988[3]	(c)
$(2.9\pm0.4)\times10^{-12}$	298		
$(5.4\pm1.1)\times10^{-12}$	300	Jenkin *et al.*, 1988[4]	(d)
Reviews and Evaluations			
$7.7\times10^{-14}\exp(1300/T)$	275–338	CODATA, 1984[5]	(e)
$7.7\times10^{-14}\exp(1300/T)$	200–300	NASA, 1985[6]	(e)
$7.7\times10^{-14}\exp(1300/T)$	200–300	NASA, 1987[7]	(f)

Comments

(a) Flash photolysis—UV absorption study involving Cl_2–CH_3OH–CH_4–O_2–N_2 mixtures at pressures of 400–600 Torr. $\sigma(HO_2)$ and $\sigma(CH_3O_2)$ were determined over the wavelength range 200–270 nm and the relative values were normalized to the value $\sigma(HO_2) = 4.9\times10^{-18}$ cm^2 molecule^{-1} at 210 nm leading to $\sigma(CH_3O_2) = 4.4\times10^{-18}$ cm^2 molecule^{-1} at 240 nm. k determined from measurements of $\sigma(HO_2)$ at 210 and $\sigma(CH_3O_2)$ at 240 nm.

(b) Flash photolysis—UV absorption study involving Cl_2–CH_3OH–CH_4–O_2–N_2 mixtures at pressures of 25–600 Torr. $\sigma(HO_2)$ and $\sigma(CH_3O_2)$ were determined over the wavelength range 215–280 nm. At 250 nm $\sigma(CH_3O_2) = 3.3\times10^{-18}$ cm^3 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. k was shown to be independent of the presence of H_2O vapor (~10 Torr).

(c) Same procedure and data analysis as for comment (b) but experiments carried out at total pressures of 100 Torr in the absence of H_2O vapor.

(d) Molecular modulation spectrometry, HO_2 and CH_3O_2 generated simultaneously by photolysis of Cl_2 in the presence of CH_4–H_2O_2–O_2 mixtures. HO_2 monitored by infrared absorption with a tunable diode laser and CH_3O_2 monitored by UV absorption at 260 nm $\sigma(CH_3O_2) = 4.25\times10^{-18}$ cm^3 molecule^{-1} was determined at 250 nm. k determined from observed perturbation of the second-order kinetics of the HO_2 self-reaction when CH_3O_2 was present in large excess. Experiments carried out at a total pressure of 10 Torr. Similar experiments on mixtures of Cl_2–H_2–CH_4–O_2 were performed at 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 10 Torr.

(e) Based on data of Cox and Tyndall.[8]

(f) Based on data of Cox and Tyndall and of McAdam *et al.*[1]

Preferred Values

$k = 4.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.7 \times 10^{-13}$ exp(1000/T) cm^3 molecule^{-1} s^{-1} over range 250–380 K.

Reliability

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

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

Comments on Preferred Values

The recent room-temperature data of McAdam *et al.*[1] and of Jenkin *et al.*[4] are in good agreement with the earlier study of Cox and Tyndall,[8] who employed the molecular modulation technique with UV absorption detection of the radicals. The value of McAdam *et al.*[1] has subsequently been revised downwards to $k = 3.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K owing to an error in the analysis [B. Veyret (private communication)]. The revised value is closer to that reported by Kurylo *et al.*[2] and by Dagaut *et al.*,[3] who also found a significantly lower negative temperature coefficient than that found earlier.[8] Part of the reason for the discrepancies arises from the use of different values for the absolute cross sections for HO_2 and CH_3O_2 at the monitoring wavelengths employed. Quantitative reconcilation of the data from the different studies is not feasible because of the complex kinetics in the experimental systems, as discussed by Dagaut *et al.*[3] and by Jenkin *et al.*[4]

The preferred rate coefficient at 298 K is a mean of the values of Dagaut *et al.*,[3] Jenkin *et al.*,[4] and Cox and Tyndall.[8] The recommended temperature coefficient is obtained by a rounded-off average of the E/R values from the two temperature dependence studies, with the A-Factor adjusted to the preferred value of k_{298}.

In studies of the system $Cl_2/CD_4/CH_3OH/O_2$, Jenkin *et al.*[4] have obtained evidence for the occurrence of the reaction, $CD_3O_2 + HO_2 \rightarrow DCDO + HDO + O_2$ from measurements of the product HDO by diode laser spectroscopy. They suggest that ~40% of the $CD_3O_2 + HO_2$ reaction proceeds by this channel. A similar channel $CH_3O_2 + HO_2 \rightarrow HCHO + H_2O + O_2$ could help to explain the large discrepancies between the rate of the $CH_3O_2 + HO_2$ reaction measured from CH_3OOH formation and from the direct methods as discussed previously.[9] The studies of Kurylo *et al.*[2] and of Jenkin *et al.*[4] both show that the rate coefficient is independent of pressure over the range 10–760 Torr.

References

[1] K. McAdam, B. Veyret, and R. Lesclaux, Chem. Phys. Lett. **133**, 39 (1987).
[2] M. J. Kurylo, P. Dagaut, T. J. Wallington, and D. M. Neuman, Chem. Phys. Lett. **139**, 513 (1987).
[3] P. Dagaut, T. J. Wallington, and M. J. Kurylo, J. Phys. Chem. **92**, 3833 (1988).
[4] M. E. Jenkin, R. A. Cox, G. D. Hayman, and L. J. Whyte, J. Chem. Soc. Faraday Trans. 2 **84**, 913 (1988).
[5] CODATA Supplement II, 1984 (See References in Introduction).
[6] NASA Evaluation No. 7, 1985 (See References in Introduction).
[7] NASA Evaluation No. 8, 1987 (See References in Introduction).
[8] R. A. Cox and G. S. Tyndall, J. Chem. Soc. Faraday Trans. 2, **76**, 153 (1980).
[9] CODATA Supplement I, 1982 (See References in Introduction).

$HO_2 + C_2H_5O_2 \rightarrow O_2 + C_2H_5O_2H$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.3 \pm 0.9) \times 10^{-12}$	295	Cattell *et al.*, 1986[1]	(a)
$(5.6 \pm 2.4) \times 10^{-13}$ exp[$+650 \pm 125)/T$]	248–380	Dagaut Wallington, and Kurylo, 1988[2]	(b)
$(5.3 \pm 1.0) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(1.5 \pm 0.5) \times 10^{-12}$	298	Niki *et al.*, 1982[3]	(c)

Comments

(a) Molecular modulation spectrometry, HO_2 and $C_2H_5O_2$, generated simultaneously by photolysis of Cl_2 in the presence of C_2H_6–CH_3OH–O_2–N_2 mixtures at pressures of 2.4 Torr. HO_2 monitored by infrared absorption with a tunable diode laser and $C_2H_5O_2$ monitored by UV absorption at 260 nm. k determined from 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 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 25–400 Torr. Composite transient absorption decay curves for HO_2 and $C_2H_5O_2$ were measured at 230, 250, and 280 nm. Kinetic analysis derived from computer modeling of experimental data.

(c) FTIR spectroscopic study of the product formation in the photolysis of mixtures of Cl_2–C_2H_6–O_2 and $(C_2H_5)_2N_2$–O_2 at 700 Torr. k derived from computer simulation of proposed mechanism.

Preferred Values

$k = 5.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.5 \times 10^{-13}$ exp(650/T) cm^3 molecule^{-1} s^{-1} over range 240–380 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The two recent direct studies[1,2] of this rate coefficient are in good agreement at 298 K, and the preferred value is the mean of these data.

The rate coefficient reported by Niki *et al.*[3] is considerably lower than the preferred value but it is derived on the basis of a much less direct technique.

The preferred temperature dependence of the rate coefficient is based on the data of Dagaut *et al.* but this requires further experimental confirmation.

The experiments of Cattell *et al.*[1] indicate that the rate coefficient is independent of total pressure based on measurements at 2.4 and 760 Torr.

References

[1] F. C. Cattell, J. Cavanagh, R. A. Cox, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. 2 **82**, 199 (1986).
[2] P. Dagaut, T. J. Wallington, and M. J. Kurylo, J. Phys. Chem. **92**, 3836 (1988).
[3] H. Niki, P. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **86**, 3825 (1982).

$HO_2 + HCHO \rightarrow HOCH_2OO$

$\Delta H^\circ = -98.1$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.1 \pm 0.4) \times 10^{-13}$	273	Barnes *et al.*, 1985[1]	(a)
$7.7 \times 10^{-15} \exp(625 \pm 550/T)$	275–333	Veyret *et al.*, 1989[2]	(b)
$(6.0 \pm 0.7) \times 10^{-14}$	295		
Reviews and Evaluations			
4.5×10^{-14}	298	CODATA, 1984[3]	(c)
4.5×10^{-14}	298	NASA, 1985[4]	(c)
4.5×10^{-14}	298	NASA, 1988[5]	(d)

Comments

(a) FTIR spectroscopic study in a 420 ℓ reaction chamber. HO_2 generated from the thermal decomposition of HO_2NO_2 in the presence of HCHO, NO_2, and synthetic air at a total pressure of 400 Torr. k 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 $[HOCH_2O_2]$ at total pressures of 85–170 Torr. k obtained from a computer simulation of the absorption profiles based on a mechanism of five elementary reactions.

(c) Average value of data of Su *et al.*,[6] ($k = 1.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}) and of Veyret *et al.*[7] ($k = 7.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}).

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 range 275–333 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 600$ K.

Comments on Preferred Values

The most recent 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.*[7] The preferred rate equation is derived by taking an average value of the rate coefficients of Barnes *et al.* [$k(273\ \text{K}) = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}] and of Veyret *et al.*[2] [$k(275\ \text{K}) = 8.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}] together with the 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. Reiner, F. Zabel, and H. Niki, Chem. Phys. Lett. **115**, 1 (1985).
[2] B. Veyret, R. Lesclaux, M. T. Rayez, R. A. Cox, and G. K. Moortgat, J. Phys. Chem. **93**, 2368 (1989).
[3] CODATA Supplement II, 1984 (See References in Introduction).
[4] NASA Evaluation No 7, 1985 (See References in Introduction).
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[6] F-Su, J. G. Calvert, J. H. Shaw, H. Niki, P. D. Maker, C. M. Savage, and L. Breitenbach, Chem. Phys. Lett. **65**, 221 (1979).
[7] B. Veyret, J. C. Rayez, and R. Lesclaux, J. Phys. Chem. **86**, 3424 (1982).

$HOCH_2OO \rightarrow HO_2 + HCHO$

$\Delta H^\circ = 98.1$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.5	298	Su, Calvert, and Shaw, 1979[1]	(a)
30	298	Veyret, Rayez, and Lesclaux, 1982[2]	(b)
20^{+20}_{-10}	273	Barnes *et al.*, 1985	(c)
$2.0\times10^{12}\exp[(-7000\pm2000)/T]$	275–333	Veyret *et al.*, 1989[4]	(d)
100 ± 50	295		

Comments

(a) Photo-oxidation of $HCHO$-Cl_2 mixtures in H_2, O_2, and N_2 or in synthetic air (total pressure ~700 Torr) studied by FTIR spectroscopy. k derived from a computer simulation of a complex system.

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

(c) FTIR spectroscopic study in a 420 ℓ reaction chamber. HO_2 generated from thermal decomposition of HO_2NO_2 in the presence of HCHO, NO_2, and synthetic air at total pressures of 400 Torr. k 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.

(d) Flash photolysis of Cl_2 in 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 85–170 Torr. k obtained from a computer simulation of the absorption profiles based on a mechanism of five elementary reactions.

Preferred Values

$k = 1.5\times10^2$ s^{-1} at 298 K.

$k = 2.4\times10^{12}\exp(-7000/T)$ s^{-1} over range 275–333 K.

Reliability

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

$\Delta(E/R) = \pm2000$ K.

Comments on Preferred Values

The studies of Barnes *et al.*[1] and of Veyret *et al.*[4] are in good agreement regarding the rate coefficient of this reaction. The preferred rate equation has been obtained by taking the average of the rate coefficients at 273 K from these studies together with the E/R determined by Veyret *et al.*[4]

It should be pointed out that the equilibrium constant for the reaction $HO_2 + HCHO \rightleftharpoons HOCH_2O_2$ $(1, -1)$, $K_1 = 5.2\times10^{-16}$ cm^3 molecule^{-1} at 298 K, derived from the kinetic study of Veyret *et al.*,[4] which is identical to the value obtained from our recommended data for k_1 and k_{-1}, is in excellent agreement with the value $K_1 = 4.0\times10^{-16}$ cm^3 molecule^{-1} at 298 K obtained independently by Burrows *et al.*[5] from molecular modulation studies. The above value of K_1 is, however, considerably smaller than the value of $k_1 = 3.4\times10^{-15}$ cm^3 molecule at 298 K reported by Zabel *et al.*,[6] from ESR spectroscopic measurements of the ratio of concentrations of HO_2 and $HOCH_2OO$ radicals in the photolysis of $HCHO/O_2$ mixtures.

References

[1] F. Su, J. G. Calvert, and J. H. Shaw, J. Phys. Chem. **83**, 3185 (1979).
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[3] I. Barnes, K. H. Becker, E. H. Fink, A Reimer, F. Zabel, and H. Niki, Chem. Phys. Lett. **115**, 1 (1985).
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$NO_3 + C_2H_2 \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.9^{+16}_{-3.7})\times10^{-13}\exp[-(2740\pm540)/T]$	296–523	Canosa-Mas *et al.*, 1988[1]	(a)
$(5.1\pm3.5)\times10^{-17}$	295		
Relative Rate Coefficients			
$\leqslant3.4\times10^{-17}$	298	Atkinson, Aschmann, and Goodman, 1987[2]	(b)

Comments

(a) Discharge flow–absorption spectroscopic detection of NO_3.

(b) Relative rate method. NO_3 radicals generated by the thermal decomposition of N_2O_5 in NO_2–air mixtures at atmospheric pressure. Relative decay rates of C_2H_2 and C_2H_4 monitored, leading to $k(NO_3 + C_2H_2)/k(NO_3 + C_2H_4) \leqslant 0.14$. Placed on an absolute basis by use of $k(NO_3 + C_2H_4) = (2.1 \pm 0.3) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k < 1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The measurement of rate coefficients for low reactivity organics is complicated by the possibility of secondary reactions, leading to erroneously high measured rate coefficients. The relative rate measurements[2] 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 is confirmatory data for the temperature dependence of this rate coefficient, no temperature dependence is recommended.

References

[1] C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2 **84**, 247, 263 (1988).

[2] R. Atkinson, S. M. Aschmann, and M. A. Goodman, Int. J. Chem. Kinet. **19**, 299 (1987).

$NO_3 + C_2H_4 \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.29^{+2.9}_{-2.0} \times 10^{-13} \exp[-(3100 \pm 144)/T]$	295–523	Canosa-Mas *et al.*, 1988[1]	(a)
$(1.85 \pm 0.24) \times 10^{-16}$	295		
Relative Rate Coefficients			
$(9.3 \pm 1.0) \times 10^{-16}$	300	Japar and Niki, 1975[2]	(b)
$(1.0 \pm 0.5) \times 10^{-16}$	298	Atkinson *et al.*, 1984[3]	(c)
$(2.14 \pm 0.20) \times 10^{-16}$	296	Atkinson, Aschmann, and Pitts, 1988[4]	(d)

Comments

(a) Discharge flow–visible absorption spectroscopic detection of NO_3.

(b) Derived from the measured decays of C_2H_4 in N_2O_5–NO_3–NO_2–C_2H_4–O_2–Ar mixtures at 750 Torr total pressure, by computer simulation of a 5-reaction system. The rate coefficient obtained depends on the equilibrium constant for the reactions $NO_2 + NO_3 \rightarrow N_2O_5$. The cited rate coefficient of $(9.3 \pm 1.0) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} was derived using an equilibrium constant of 1.25×10^{-11} cm^3 molecule^{-1} at 300 K.

(c) Relative rate method, in which the relative decay rates of C_2H_4 and C_3H_6 and of C_3H_6 and *trans*-2-butene were measured by gas chromatography in N_2O_5–NO_3–NO_2–air mixtures at atmospheric pressure. The measured rate coefficient ratios of $k(NO_3 + C_2H_4)/k(NO_3 +$ propene$) = 0.013 \pm 0.006$ and $k(NO_3 +$ propene$)/k(NO_3 +$ *trans*-2-butene$) = 0.019 \pm 0.005$ have been combined and placed on an absolute basis by use of $k(NO_3 +$ *trans*-2-butene$) = 3.87 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[5,6]

In addition, the enhanced decay rates of N_2O_5 were monitored by FT-IR absorption spectroscopy in N_2O_5–NO_3–NO_2–C_2H_4–air mixtures at atmospheric pressure, and $k(NO_3 + C_2H_4)$ was determined relative to the equilibrium constant for the reactions $NO_2 + NO_3 \rightleftarrows N_2O_5$. Use of an equilibrium constant of 3.44×10^{-11} cm^3 molecule^{-1} for these reactions[7] leads to a rate coefficient of $(1.4 \pm 0.5) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}, in good agreement with the relative rate measurements.

(d) Relative rate method. The relative decay rates of several sets of organics were monitored by gas chromatography in N_2O_5–NO_2–air mixtures at atmospheric pressure. By combining the rate coefficient ratios for *trans*-2-butene and bicyclo[2.2.2]-2-octene, bicyclo[2.2.2]-2-octene and thiophene, thiophene and propene, propene and tetrahydrofuran, tetrahydrofuran and 2,3-dimethylbutane, and 2,3-dimethylbutane and ethene, a rate coefficient ratio of $k(NO_3 +$ ethene$)/k(NO_3 +$ *trans*-2-butene$) = (5.54 \pm 0.50) \times 10^{-4}$ was obtained. Placed on an absolute basis by use of $k(NO_3 +$ *trans*-2-butene$) = 3.87 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[5,6]

Preferred Values

$k = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The preferred value is based upon the most recent rate coefficient study of Atkinson *et al.*[4] (which supersedes the earlier work[3] of this group) and the absolute room temperature rate coefficient for NO_3 + *trans*-2-butene of Ravishankara and Mauldin[5] and Dlugokencky and Howard.[6] The preferred rate coefficient is in good agreement with the absolute measurement of Canosa-Mas *et al.*,[1] but disagrees with that measured by Japar and Niki[2] by almost an order of magnitude.

No recommendation is made concerning the temperature dependence of this rate coefficient. The reaction is expected to proceed via NO_3 radical addition to the carbon-carbon double bond.[2,3]

References

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$NO_3 + C_3H_6 \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3 \pm 0.75) \times 10^{-15}$	300	Morris and Niki, 1974[1]	(a)
$(5.3 \pm 0.3) \times 10^{-15}$	300	Japar and Niki, 1975[2]	(a)
$(7.4 \pm 2.0) \times 10^{-15}$	298	Atkinson *et al.*, 1984[3]	(b)
$(9.4 \pm 0.5) \times 10^{-15}$	296	Atkinson, Aschmann, and Pitts, 1988	(c)

Comments

(a) Relative rate method. Decay of N_2O_5 monitored by infrared absorption spectroscopy in N_2O_5–NO_2–NO_3–C_3H_6–O_2–Ar mixtures at 750 Torr total pressure. The rate coefficient derived for C_3H_6 is dependent on the equilibrium constant for the reactions $NO_2 + NO_3 \rightleftarrows N_2O_5$. The cited value in the table uses an equilibrium constant of 1.25×10^{-11} cm^3 molecule^{-1} for this equilibrium constant.

(b) Relative rate method in which the decay rate of C_3H_6 was monitored relative to that of *trans*-2-butene in N_2O_5–NO_2–NO_3 mixtures by gas chromatography. The measured rate coefficient ratio of $k(NO_3 + \text{propene})/k(NO_3 + \textit{trans}\text{-2-butene})$ of 0.019 ± 0.005 has been placed on an absolute basis by use of $k(NO_3 + \textit{trans}\text{-2-butene}) = 3.87 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[5,6] Additionally, N_2O_5 decay rates were monitored by FT–IR absorption spectroscopy in N_2O_5–NO_2–NO_3–C_3H_6–air mixtures at atmospheric pressure. The rate coefficient is then relative to the equilibrium constant for the reactions $NO_2 + NO_3 \rightleftarrows N_2O_5$. Use of an equilibrium constant of 3.44×10^{-11} cm^3 molecule^{-1} for these reactions[7] leads to a rate coefficient of $(7.6 \pm 1.6) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, in good agreement with the relative rate measurements.

(c) Relative rate method. The relative decay rates of several sets of organics were monitored in N_2O_5–NO_2–air mixtures at atmospheric pressure by gas chromatography. By combining the rate coefficient ratios for *trans*-2-butene and bicyclo[2.2.2]-2-octene, bicyclo[2.2.2]-2-octene and thiophene, and thiophene and propene, a rate coefficient ratio of $k(NO_3 + \text{propene})/k(NO_3 + \textit{trans}\text{-2-butene}) = 0.0243 \pm 0.0012$ was obtained. Placed on an absolute basis by use of $k(NO_3 + \textit{trans}\text{-2-butene}) = 3.87 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[5,6]

Preferred Values

$k = 9.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

Based on the most recent relative rate study of Atkinson *et al.*,[4] which supersedes the earlier work from this group[3] and which is in reasonable agreement with the earlier studies of Niki and co-workers[1,2] when the differing equilibrium constants used for the $NO_2 + NO_3 \rightleftarrows N_2O_5$ reactions are taken into account. The reaction is expected to proceed by NO_3 radical addition to the carbon-carbon double bond.[1-3,8,9]

References

[1] E. D. Morris, Jr. and H. Niki, J. Phys. Chem. **78**, 1337 (1974).

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$NO_3 + HCHO \rightarrow HNO_3 + HCO$

$\Delta H^\circ = -62.1$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(5.8 \pm 0.5) \times 10^{-16}$	298	Atkinson *et al.*, 1984[1]	(a)
$(6.3 \pm 1.1) \times 10^{-16}$	298	Cantrell *et al.*, 1985[2]	(b)
5.4×10^{-16}	298	Hjorth *et al.*, 1988[3]	(c)
Reviews and Evaluations			
6×10^{-16}	298	NASA, 1985[4]	(d)
6.0×10^{-16}	298	NASA, 1987[5]	(d)

Comments

(a) Relative rate method. N_2O_5 decay rates monitored as a function of the $HCHO/NO_2$ concentration ratio. The rate coefficient derived is dependent on the value of the equilibrium constant for the reactions $NO_2 + NO_3 \rightleftarrows N_2O_5$. An equilibrium constant of $K = 3.44 \times 10^{-11}$ cm^3 molecule^{-1} at 298 K determined by Tuazon *et al.*[6] (which allows the analogous data for *trans*-2-butene to be placed in agreement with the recent absolute rate coefficients of Ravishankara and Mauldin[7] and Dlugokencky and Howard[8]) has been used to place the rate coefficient on an absolute basis.

(b) Derived from computer fits of time-concentration data for reactants and products, monitored by FT–IR absorption spectroscopy, in O_3–NO_2–HCHO–O_2–N_2 mixtures. For five of the nine experiments the rate coefficient derived was dependent on the equilibrium constant for the reactions $NO_2 + NO_3 \rightleftarrows N_2O_5$. An equilibrium constant of 2.34×10^{-11} cm^3 molecule^{-1} was used, this being a factor of 1.5 lower than that used to derive the data of Atkinson *et al.*[1] above. For four experiments in which the NO_3 radical was monitored, the rate coefficient is not dependent on the equilibrium constant for the reactions $NO_2 + NO_3 \rightleftarrows N_2O_5$, and a rate coefficient of 5.8×10^{-16} cm^3 molecule^{-1} s^{-1} was obtained.

(c) Derived from computer fits of time-concentration data for reactants and products, monitored by FT–IR absorption spectroscopy, in O_3–NO_2–HCHO–O_2–N_2 and N_2O_5–NO_2–HCHO–O_2–N_2 mixtures. The rate coefficient derived is dependent on the equilibrium constant for the reactions $NO_2 + NO_3 \rightleftarrows N_2O_5$. An equilibrium constant of 2.34×10^{-11} cm^3 molecule^{-1} was used.

(d) Based upon the rate coefficients of Atkinson *et al.*[1] and Cantrell *et al.*[2]

Preferred Values

$k = 6 \times 10^{-16}$ 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 Cantrell *et al.*,[2] Atkinson *et al.*,[1] and Hjorth *et al.*[3] disagree by a factor of ~1.5 when the same equilibrium constant for the reactions $NO_2 + NO_3 \rightleftarrows N_2O_5$ is used to place the rate coefficients on an absolute basis. However, the rate coefficient obtained by Cantrell *et al.*[2] from experiments which were independent of this equilibrium constant agree well with that derived from the Atkinson *et al.*[1] data using the equilibrium constant which yields agreement between the relative[1] and absolute[7,8] measurements for NO_3 + *trans*-2-butene.

Accordingly, a rate coefficient of 6×10^{-16} cm^3 molecule^{-1} s^{-1} is recommended, with the uncertainty limits reflecting the need for an absolute measurement.

References

[1] R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **88**, 1210 (1984).

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[8] E. Dlugokencky and C. J. Howard, J. Phys. Chem., **93**, 1091 (1989).

$NO_3 + CH_3CHO \rightarrow HNO_3 + CH_3CO$

$\Delta H^\circ = -66.4$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.44 \pm 0.18) \times 10^{-12} \exp[-(1860 \pm 300)/T]$	264–374	Dlugokencky and Howard, 1989[1]	(a)
$(2.74 \pm 0.33) \times 10^{-15}$	298		
Relative Rate Coefficients			
$(1.2 \pm 0.3) \times 10^{-15}$	300	Morris and Niki, 1974[2]	(b)
$(2.5 \pm 0.8) \times 10^{-15}$	298	Atkinson *et al.*, 1984[3]	(c)
$(2.1 \pm 0.4) \times 10^{-15}$	299	Cantrell *et al.*, 1986[4]	(d)
Reviews and Evaluations			
$1.4 \times 10^{-12} \exp(-1900/T)$	264–374	NASA, 1987[5]	(e)

Comments

(a) Flow system with laser-induced fluorescence detection of NO_3.

(b) Relative rate method. NO_3 radicals generated from the thermal decomposition of N_2O_5 in O_2/Ar mixtures at 750 Torr total pressure. Decays of N_2O_5 monitored by infrared absorption spectroscopy in the presence of excess CH_3CHO. Placed on an absolute basis by use of an equilibrium constant for the $NO_2 + NO_3 \rightleftarrows N_2O_5$ reactions of 1.25×10^{-11} cm^3 molecule^{-1}.

(c) Relative rate method. NO_3 radicals generated from the thermal decomposition of N_2O_5 in air at 740 Torr total pressure, and the decays of N_2O_5 in the presence of excess CH_3CHO monitored by FT–IR absorption spectroscopy. Placed on an absolute basis by use of an equilibrium constant for the $NO_2 + NO_3 \rightleftarrows H_2O_5$ reactions of $(3.44 \pm 0.81) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[6]

(d) NO_3 radicals generated from the thermal decomposition of N_2O_5 in synthetic air at 700 Torr total pressure. Reactants and products monitored by FT–IR absorption spectroscopy, and their time-concentration profiles fitted by computer modeling, using an equilibrium constant for the $NO_2 + NO_3 \rightleftarrows N_2O_5$ reactions of 2.0×10^{-11} cm^3 molecule^{-1} at 299 K.

(e) The 298 K value was derived from the rate coefficient data of Atkinson *et al.*,[3] Cantrell *et al.*,[4] and Dlugokencky and Howard.[1] The temperature dependence of Dlugokencky and Howard[1] was utilized with the A factor being adjusted to yield the preferred 298 K value.

Preferred Values

$k = 2.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.4 \times 10^{-12} \exp(-1860/T)$ cm^3 molecule^{-1} s^{-1} over the range 260–370 K.

Reliability

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

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

Comments on Preferred Value

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] (when linearly corrected to be consistent with recent values of the equilibrium constant for the $NO_2 + NO_3 \rightleftarrows N_2O_5$ reactions), Atkinson *et al.*[3] and Cantrell *et al.*[4] are in reasonable agreement with this preferred value. However, because of the significant uncertainties in this equilibrium constant,[5,6] these relative rate coefficient data were not used in the evaluation of the preferred rate coefficient.

References

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$NO_3 + CH_3OH \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leqslant 6 \times 10^{-16}$	298	Wallington *et al.*, 1987[1]	(a)

Comments

(a) Flash photolysis–absorption spectroscopic detection of NO_3.

Preferred Values

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

Comments on Preferred Value

The preferred value is based on the only study carried out to date.[1] A somewhat higher upper limit is recommended.

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. 19, 243 (1987).

$NO_3 + C_2H_5OH \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leqslant 9 \times 10^{-16}$	298	Wallington *et al.*, 1987[1]	(a)

Comments

(a) Flash photolysis–absorption spectroscopic detection of NO_3.

Preferred Values

$k < 2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

The preferred value is based on the only study carried out to date.[1] A somewhat higher upper limit is recommended rather than cited by Wallington *et al.*[1]

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. 19, 243 (1987).

$NO_3 + i\text{-}C_3H_7OH \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leqslant 2.3 \times 10^{-15}$	298	Wallington *et al.*, 1987[1]	(a)

Comments

(a) Flash photolysis–absorption spectroscopic detection of NO_3.

Preferred Values

$k < 5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

The preferred value is based on the only study carried out to date.[1] A somewhat higher upper limit is recommended rather than cited by Wallington *et al.*[1]

References

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

$\Delta H^\circ = -122.6$ kJ mol^{-1}

Low-Pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.0 \pm 1.0) \times 10^{-31}$[Ar]	298	Cobos *et al.* 1985[1]	(a)
$(8.0 \pm 1.0) \times 10^{-31}$ [N$_2$]	298		
$(4.8 \pm 0.6) \times 10^{-31}$ [Ar]	298	Pilling and Smith, 1985[2]	(b)
$(1.0 \pm 0.3) \times 10^{-30}(T/300)^{-3.3 \pm 0.4}$	334–582	Keiffer, Pilling, and Smith, 1987[3]	(c)
Relative Rate Coefficients			
8.0×10^{-32} exp(243/T) [Ar]	230–568	Pratt and Wood, 1984[4]	(d)
1.8×10^{-31} [Ar]	298		
Reviews and Evaluations			
$6 \times 10^{-31}(T/300)^{-2}$[N$_2$]	200–300	CODATA, 1984[5]	(e)
$4.5 \times 10^{-31}(T/300)^{-2}$ [air]	200–300	NASA, 1988[8]	(f)

Comments

(a) Laser flash photolysis study with azomethane as the CH_3 source and following CH_3 by UV absorption. Pressures of bath gases N_2, Ar, and O_2 varied between 0.2 and 150 atm. Falloff curves constructed with $F_c = 0.27$, $N = 1.47$, and $k_\infty = 2.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Due to the low value of the theoretically modeled F_c, a high limiting value of k_0 is extracted from the measurements.

(b) Laser flash photolysis study with azomethane as CH_3 source and following CH_3 by UV absorption. Pressures of bath gas Ar varied between 3.2 and 490 Torr. Falloff curves constructed using $F_c = 0.57$ (including strong and weak collision contributions).

(c) Laser flash photolysis study with acetone as the CH_3 source; CH_3 monitored by UV absorption. Measurements in the pressure range 20–600 Torr. Falloff curves constructed with $F_c \approx 0.6$, various fitting procedures applied and discussed.

(d) Flow–discharge system at pressures of 2 to 10 Torr. CH_3 produced from H + C_2H_4 reaction. Reaction rates determined from the effect of added O_2 on the radical combination products. Falloff curves constructed assuming that k_∞ and F_c are independent of temperature.

(e) Based largely on data of Plumb and Ryan[6] and Selzer and Bayes.[7]

(f) Fitted with $F_c = 0.6$. Using smaller F_c, such as given in Ref. 1, a higher k_0 value would be obtained. At pressures below 1 atm, representations 5 and 8 fit the experimental data equally well.

Preferred Values

$k_0 = 8 \times 10^{-31}(T/300)^{-3.3}$[N$_2$] cm^3 molecule^{-1} s^{-1} over the range 200–600 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

Although the experimental data now give a satisfactory appearance of the falloff curve, the extrapolation toward the low-pressure limit depends strongly on the theoretical model employed and remains uncertain. Simple models have led to F_c values near 0.6, whereas the detailed modeling in Ref. 1 suggests about a factor of 2 lower value at 300 K. For the pressure range 0.001–1 atm and the temperature range 200–300 K, the present evaluation using $F_c = 0.27$ at 300 K and the NASA evaluation using $F_c = 0.6$ with their correspondingly different k_0 values reproduce the experimental data equally well. A detailed modeling of the temperature dependence of the reaction, which will result in strongly T-dependent F_c values below 300 K, appears necessary. This modeling should take into account the new study of the thermochemistry of the reaction from Ref. 9.

High-pressure rate coefficient
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.3) \times 10^{-12}(T/300)^{0.94}$	200–400	Cobos *et al.*, 1985[1]	(a)
$(1.05 \pm 0.12) \times 10^{-12}$	298	Pilling and Smith, 1985[2]	(b)
$(1.2 \pm 0.2) \times 10^{-12}(T/300)^{1.2 \pm 0.4}$	334–582	Keiffer, Pilling, and Smith, 1987[3]	(c)
Reviews and Evaluations			
1.8×10^{-12}	200–300	CODATA, 1984[5]	(d)
$1.8 \times 10^{-12}(T/300)^{-1.7}$	200–300	NASA, 1988[8]	(e)

Comments

(a) See comment (a) for k_0. The given k_∞ value is fairly insensitive to the chosen F_c values of the falloff extrapolation. The T dependence is from theoretical modeling.

(b) See comment (b) for k_0. The discrepancy between the given k_∞ value and the high pressure measurements from Ref. 1 is attributed to the neglect of a $CH_3 + CH_3O_2 \rightarrow 2CH_3O$ contribution in Ref. 1.

(c) See comment (c) for k_0.

(d) Based on preliminary results from Ref. 1.

(e) Based on date from Ref. 1 and an estimate of the temperature coefficient.

Preferred Values

$k_\infty = 2.2 \times 10^{-12}(T/300)^1$ cm^3 molecule^{-1} s^{-1} over the range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$.

$\Delta n = \pm 1$.

Comments on Preferred Values

The discrepancy between the data from Ref. 1 and Refs. 2 and 3 is due to the assumption of a contribution from the reaction $CH_3 + CH_3O_2 \rightarrow 2CH_3O$ in Refs. 2 and 3. As long as this is not confirmed, we prefer the direct measurement from Ref. 1. The measured T dependence from Ref. 3 agrees well with the theoretically predicted behavior from Ref. 1. It is in contrast to the estimate from Ref. 8.

Intermediate Falloff Range

The preferred k_0 values depend strongly on the chosen F_c values of 0.27 for 300 K in this work and 0.6 in Refs. 2, 3, and 8. Since measurements down to sufficiently low pressures are not available today and the theoretical models depend on a number of uncertain factors, no unambiguous choice can be made. The data for 300 K are equally well reproduced by either (k_0, F_c) representations. However, the temperature dependences of the low-pressure ends of the falloff curves are not well characterized as yet.

References

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$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$

$\Delta H^\circ = -50.2$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
2×10^{-13}	298	CODATA, 1984[1]	(a)
$3.3 \times 10^{-12} \exp(-2510/T)$	700–2000	Warnatz, 1984[2]	(b)
$1.4 \times 10^{-12} \exp(-1950/T)$	300–2500	Tsang and Hampson, 1986[3]	(b,c)

Comments

(a) Based on low-pressure data from Ref. 4, obtained in a study of the reaction $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$.

(b) Includes high-temperature data from shock tube and other studies.

(c) Based on data from Ref. 5.

Preferred Values

$k = 1.4 \times 10^{-12} \exp(-1950/T)$ cm^3 molecule^{-1} s^{-1} over the range 300–2500 K.

$k < 2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at $T \geqslant 700$ K.

$\Delta (E/R) = \pm 600$ K.

Comments on Preferred Values

The question of a contribution of this reaction to the overall reaction between $C_2H_5 + O_2 + M$ remains unsettled, although some new information on this reaction at room temperature[6] is coming up. The rate data obtained in the temperature range 600–800 K (e.g., from Refs. 5, 7, and 8) are difficult to extrapolate to lower temperatures because of the overlapping contributions from this reaction and the addition process $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ in its falloff range, followed by further reactions of $C_2H_5O_2$ radicals.[9] As long as no direct and unambiguous information on this reaction near room temperature is available, we base the present recommendation on the extrapolation of high-temperature results.

References

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

$\Delta H^\circ = -124.5$ kJ mol^{-1}

Comments

The reaction has been studied[1] by pulse radiolysis in H_2 at 1 atm over the temperature range 298–400 K. C_2H_5 radicals were generated via $H + C_2H_4$ from the radiolysis of H_2, the progress of reaction was monitored via $C_2H_5O_2$ absorption at 240 nm. A rate coefficient of $k = 1.3 \times 10^{-12} \exp(420/T)$ cm^3 molecule^{-1} s^{-1} was derived corresponding to k (298 K) $= 5.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. While the room-temperature value of k essentially agrees with our earlier preferred value[2] of k near to the high-presure limit, the negative temperature coefficient from Ref. 1 is due to falloff effects such as represented in Ref. 2. A theoretical modeling of the reaction can now be based on improved thermochemical information from Ref. 3 ($\Delta H^\circ = -147.3$ kJ mol^{-1}). The new data do not change our earlier recommendation.

References

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[2] CODATA Supplement II, 1984 (See References in Introduction).
[3] I. R. Slagle, E. Ratajczak, and D. Gutman, J. Phys. Chem. **90**, 402 (1986).

$n\text{-}C_3H_7 + O_2 + M \rightarrow n\text{-}C_3H_7O_2 + M$

Comments

The reaction was studied in Ref. 1 over the temperature range 297–635 K in a flow system using photoionization mass spectrometric detection of n-C_3H_7 radicals. The radicals were formed by CO_2 laser photolysis of $C_6F_7C_4H_9$. Over the range of carrier gas pressures from 0.4 to 6.8 Torr in He or N_2 only weak pressure dependences were observed. However, the rate coefficient at the highest pressures decreases from $k_\infty = 6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 297 K (in agreement with our earlier evaluation[2] based on Ref. 3) to 2.8×10^{-13} cm^3 molecule^{-1} s^{-1} at 635 K. The behavior has to be explained by increasing falloff at increasing temperatures, and the appearance of a pressure independent contribution leading to $C_3H_6 + HO_2$ at higher temperatures. The new data do not change our earlier recommendation.

References

[1] I. R. Slagle, J.-Y. Park, and D. Gutman, *20th International Symposium on Combustion* (Combustion Institute, Pittsburgh, PA, 1985), p. 733.
[2] CODATA Supplement II, 1984 (See References in the Introduction).
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$i\text{-}C_3H_7 + O_2 + M \rightarrow i\text{-}C_3H_7O_2 + M$

$\Delta H^\circ = -157.7$ kJ mol^{-1}

Comments

In a pulse radiolysis study[1] in H_2 at 1 atm, i-C_3H_7 was generated by the reaction $H + C_3H_6$ and monitored by UV absorption at 253 nm. An absorption spectrum of i-$C_3H_7O_2$ was observed on addition of O_2 to the system. A simulation of the i-C_3H_7 decay curves led to a value of the rate constant $k_\infty = (8.3 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in near agreement with our earlier recommendation[2] of $k_\infty = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (based on Ref. 3), which remains unaltered. Direct studies[4] of the i-$C_3H_7 + O_2 = i$-$C_3H_7O_2$ equilibrium gave the ΔH° value indicated above.

References

[1] J. Munk, P. Pagsberg, E. Ratajczak, and A. Sillescu, Chem. Phys. Lett. **132**, 417 (1986).
[2] CODATA Supplement II, 1984 (See References in Introduction).
[3] R. P. Ruiz and K. D. Bayes, J. Phys. Chem. **88**, 2592 (1984).
[4] I. R. Slagle, E. Ratajczak, M. C. Heaven, D. Gutman, and A. F. Wagner, J. Am. Chem. Soc. **107**, 1838 (1985).

$CH_3O + O_2 \rightarrow HCHO + HO_2$

$\Delta H^\circ = -111.6$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.5 \pm 2.0) \times 10^{-14} \exp(-1000/T)$	298–450	Lorenz *et al.*, 1985[1]	(a)
1.9×10^{-15}	298		
$2.3 \times 10^{-14} (1000/T)^{-9.5} \exp(2768/T)$	298–973	Wantuck *et al.*, 1987[2]	(b)
2.1×10^{-15}	298		
Reviews and Evaluations			
$1.1 \times 10^{-13} \exp(-1310/T)$	298–630	CODATA, 1984[3]	(c)
$1.7 \times 10^{-11} \exp(-3610/T)$	300–2000	Warnatz, 1984[4]	(d)
$8.4 \times 10^{-14} \exp(-1200/T)$	200–300	NASA, 1985[5]	(c)
$3.9 \times 10^{-14} \exp(-900/T)$	200–300	NASA, 1987[6]	(e)

Comments

(a) Laser photolysis of CH_3ONO with LIF monitoring of CH_3O at pressures of 75 Torr of He. k (298 K) shown to be independent of pressure over the range 7.5–150 Torr of He.

(b) Laser photolysis of CH_3OH or CH_3ONO at 193 nm in presence of O_2 plus 25 Torr of Ar. $[CH_3O]$ monitored by LIF. Non-Arrhenius behavior observed over entire temperature range and rate coefficients were found to obey a double exponential expression.:

$$k = 1.5\times10^{-10}\exp(-6028/T) + 3.6\times10^{-14}\exp(-880/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

(c) Based on data of Gutman *et al.*[7]

(d) Includes high-temperature data from shock-tube and other studies.

(e) Based on data of Gutman *et al.*[7] and Lorenz *et al.*[1]

Preferred Values

$k = 1.9\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.2\times10^{-14}\exp(-1080/T)$ cm^3 molecule^{-1} s^{-1} over range 298–610 K.

Reliability

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

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

Comments on Preferred Values

The recent direct measurements of the rate coefficients by Lorenz *et al.*,[1] (298–450 K and of Wantuck *et al.*,[2] (298 973 K) are in good agreement with the similar measurements of Gutman *et al.*[7] (413–608 K) where the temperature ranges overlap. The preferred temperature dependence of the rate coefficient was derived from a least-mean-squares analysis of the three sets of data over the temperature range 298–608 K and is essentially in agreement wlth the most recent NASA recommendation.[6] The higher temperature measurements of Wantuck *et al.*[2] 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.[6]

References

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[4]J. Warnatz, "Rate Coefficients in the C/H/O System," in *Combustion Chemistry*, edited by W. C. Gardiner, (Springer, New York, 1984), p. 197.
[5]NASA Evaluation No. 7, 1985 (See References in Introduction).
[6]NASA Evaluation No. 8, 1987 (See References in Introduction).
[7]D. Gutman, N. Sanders, and J. E. Butler, J. Phys. Chem. **86**, 66 (1982).

$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$

$\Delta H^\circ = -134.4$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.2\pm0.4)\times10^{-13}\exp[-(924\pm94)/T]$	225–393	Zabarnick and Heicklen, 1985[1]	(a)
5.4×10^{-15}	298		
Reviews and Evaluations			
8.0×10^{-15}	298	CODATA, 1984[2]	(b)

Comments

(a) Photolysis with 366 nm radiation of C_2H_5ONO in a static system in the presence of NO, O_2 and N_2 at total pressures > 155 Torr. Rate data based on measured quantum yields of CH_3CHO product. k measured relative to $C_2H_5O + NO \rightarrow$ products, i.e., $k(C_2H_5 + O_2)/k(C_2H_5)O + NO) = 6.8\times10^{-3}\exp(-924/T)$. Above k based on $k(C_2H_5O + NO) = 1.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1} independent of temperature. This latter k is estimated on the assumptions (i) that k for the reaction $C_2H_5O + NO + M \rightarrow C_2H_5ONO + M$ will be approximately equal to that[5] for the reaction $CH_3O + NO + M \rightarrow CH_3ONO + M$, i.e., $k_\infty = 1.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K (CODATA value) and (ii) that[6] $k_d/k_c = 0.28$ at 298 K for the reactions $C_2H_5O + NO \rightarrow CH_3CHO + HNO$ (d) and $C_2H_5O + NO(+M) \rightarrow C_2H_5ONO(+M)$ (c).

(b) Based on data of Gutman *et al.*[3]

Preferred Values

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

Reliability

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

Comments on Preferred Values

The recent study of Zabarnick and Heicklen,[1] based on a complex indirect system, yields a rate coefficient at 298 K, which is in reasonable agreement with the results of Gutman *et al.* from direct LIF measurements of the decay of C_2H_5O

in the presence of O_2. This agreement, however, is dependent upon the choice of the rate coefficient for the reference reaction in the Zabarnick and Heicklen[1] system, i.e., $k(C_2H_5O + NO)$. These latter authors selected $k(C_2H_5O + NO) = 4.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K based on a study of the rate coefficient for the decomposition of C_2H_5ONO and a calculated equilibrium constant. Here we have selected a value of $k(C_2H_5O + NO)$ based on direct data for the analogous reaction $CH_3O + NO + M \rightarrow CH_3ONO + M$ and the measured[6] disproportionation-combination ratio for $C_2H_5O + NO$ of $k_d/k_c = 0.28$.

On the other hand the temperature coefficients as measured by Gutman *et al.*[3] (E/R) = 650 K) and by Zabarnick and Heicklen[1] (E/R = 924 K) are not in such good agreement, and this aspoect of the reaction requires further investigation.

References

[1]S. Zabarnick and J. Heicklen, Int. J. Chem. Kinet. **17**, 455 (1985).
[2]CODATA Supplement II, 1984 (See References in Introduction).
[3]D. Gutman, N. Sanders, and J. E. Butler, J. Phys. Chem. **86**, 66 (1982).
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[6]P. Morabito and J. Heicklen, J. Phys. Chem. **89**, 2914 (1985).

$n\text{-}C_3H_7O + O_2 \rightarrow C_2H_5CHO + HO_2$

$\Delta H^\circ = -134.2$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.3 \pm 0.8)\times10^{-13}\exp[-(879 \pm 117)/T]$	247–393	Zabarnick and Heicklen, 1985[1]	(a)
6.8×10^{-15}	298		
Reviews and Evaluations			
$4.2\times10^{-13}\exp(-2700/T)$	298	Demerjian, Kerr, and Calvert[2]	(b)

Comments

(a) Photolysis with 366 nm radiation of $n\text{-}C_3H_7ONO$ in a static system in the presence of NO, O_2, and N_2 at total pressures of > 150 Torr. Rate data based on measured quantum yields of C_2H_5CHO product. k measured relative to $n\text{-}C_3H_7O + NO \rightarrow$ products, i.e., $k(n\text{-}C_3H_7O + O_2)/k(nC_3H_7O + NO) = 6.8\times10^{-3}\exp(-879/T)$. Above k based on $k(n\text{-}C_3H_7O + NO) = 1.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} independent of temperature. This latter k is estimated on the assumptions (i) that k for the reaction $n\text{-}C_3H_7O + NO + M \rightarrow n\text{-}C_3H_7ONO + M$ will be approximately equal to that[3] for the reaction $CH_3O + NO + M \rightarrow CH_3ONO + M$, i.e., $k_\infty = 1.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K (CODATA value) and (ii) that[4] $k_d/k_c = 0.35$ for the reactions $n\text{-}C_3H_5O + NO \rightarrow C_2H_5CHO + HNO$ (d) and $n\text{-}C_3H_7O + NO(+M) \rightarrow n\text{-}C_3H_7ONO(+M)$ (c).

(b) Estimate based on an assumed A-factor for $RO + O_2$ reactions and E calculated empirically from ΔH° for the reaction.

Preferred Values

$k = 8\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The rate coefficient at 298 K derived from the Zabarnick and Heicklen[1] study, though heavily dependent upon the choice of data for the reference reaction, $n\text{-}C_3H_7O + NO \rightarrow$ products, is in line with data for other $RO_2 + O_2$ reactions obtained from direct studies. Here, we have selected k_{298} to be equal to that for the $C_2H_5O + O_2$ reaction.

The temperature coefficient determined by Zabarnick and Heicklen[1] from their relative rate system is considerably greater than either that ($E/R = 650$ K) for the $C_2H_5O + O_2$ reaction or that ($E/R = 200$ K) for the $i\text{-}C_3H_7 + O_2$ reaction, both obtained from direct studies. This aspect of the reaction requires further experimental work.

References

[1]S. Zabarnick and J. Heicklen, Int. J. Chem. Kinet. **17**, 477 (1985).
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$i\text{-}C_3H_7O + O_2 \rightarrow CH_3COCH_3 + HO_2$

$\Delta H^\circ = -150.3\ \text{kJ mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.51 \pm 0.70)\times 10^{-14}\exp[-(200 \pm 140)/T]$	294–384	Balla, Nelson, and McDonald, 1985[1]	(a)
7.72×10^{-15}	298		

Comments

(a) Pulsed laser photolysis of isopropyl nitrite at 355 nm, with LIF detection of $i\text{-}C_3H_7O$. Pressure range 1–50 Torr.

Preferred Values

$k = 8\times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.5\times 10^{-14}\exp(-200/T)$ cm^3 molecule^{-1} s^{-1} over range 290–390 K.

Reliability

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

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

Comments on Preferred Values

The results of Balla *et al.*[1] on the rate coefficient of this reaction appear reasonable in relation to data for other reactions of this type. Both the rate coefficient and temperature coefficient require confirmation.

References

[1] R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **99**, 32 (1985).

$CH_2OH + O_2 \rightarrow HCHO + HO_2$

$\Delta H^\circ = -68.1\ \text{kJ mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.4 \pm 0.4)\times 10^{-12}$	298	Wang, Suto, and Lee, 1984[1]	(a)
$(9.5 \pm 2.5)\times 10^{-12}$	298	Grotheer *et al.*, 1985[2]	(b)
$(10.6 \pm 2.5)\times 10^{-12}$	296	Dobé *et al.*, 1985[3]	(c)
$(10.5 \pm 4.7)\times 10^{-12}$	296		(d)
$(8.6 \pm 2.0)\times 10^{-12}$	298	Payne *et al.*, 1988[4]	(e)
Reviews and Evaluations			
2×10^{-12}	298	CODATA, 1984[5]	(f)
$1.7\times 10^{-11}\exp(-3600/T)$	300–2000	Warnatz, 1984[6]	(g)
2×10^{-12}	298	NASA, 1985[7]	(f)
9.6×10^{-12}	200–300	NASA, 1987[8]	(h)

Comments

(a) Discharge-flow system in which CH_2OH generated from $Cl + CH_3OH$ at total pressures of ~1.5 Torr. k derived from rate of disappearance of CH_2OH as determined via HO_2 product, in turn detected by HO photofragment emission from vacuum UV absorption by HO_2.

(b) CH_2OH generated from $Cl + CH_3OH$ in a discharge-flow system. Mass spectrometric analysis of CH_2OH in the presence of excess O_2 at total pressures of 0.3–0.9 Torr.

(c) CH_2OH generated from $F + CH_3OH$ in a discharge-flow system at total pressures of 0.52–4.9 Torr. k derived from disappearance of CH_2OH monitored by LMR spectroscopy.

(d) As for comment (c) but k derived from rate of appearance of HO_2 monitored by LMR spectroscopy.

(e) CH_2OH generated from $Cl + CH_3OH$ in a discharge-flow system at total pressures of ~1 Torr. k derived from decay of CH_2OH measured by mass spectrometry in an excess of O_2.

(f) Based on data of Radford.[9]

(g) Includes high-temperature data from shock-tube and other studies.

(h) Based on data of Grotheer *et al.*[2] and Dobé *et al.*[3]

Preferred Values

$k = 9.8\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value of k at 298 K is the mean of the data of Grotheer *et al.*,[2] Dobé *et al.*,[3] (two values) and of Payne *et al.*,[4] which are in excellent agreement. The earlier data of Radford[9] and of Wang *et al.*[1] appear to be in error arising from the high concentrations of radicals involved, which lead to mechanistic complications.

Combination of the k_{298} value from direct studies with high-temperature rate coefficients[6] indicates that the reaction could have a small negative temperature coefficient. This aspect of the system requires further investigation by direct techniques.

References

[1] W. C. Wang, M. Suto, and L. C. Lee, J. Chem. Phys. **81**, 3122 (1984).
[2] H.-H. Grotheer, G. Riekert, U. Meier, and T. Just, Ber. Bunsenges. Phys. Chem. **89**, 187 (1985).
[3] S. Dobé, F. Temps, T. Bohland, and H. Gg. Wagner, Z. Naturforschung Teil A **40**, 1289 (1985).
[4] W. A. Payne, J. Brunning, M. B. Mitchell, and L. J. Stief, Int. J. Chem. Kinet. **20**, 63 (1988).
[5] CODATA Supplement II, 1984 (See References in Introduction).
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[9] H. E. Radford, Chem. Phys. Lett. **71**, 195 (1980).

$CH_3 + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.1 \pm 1.6) \times 10^{-12} \exp[-(210 \pm 84)/T]$	243–384	Paltenghi, Ogryzlo, and Bayes, 1984[1]	(a)
$(2.53 \pm 0.54) \times 10^{-12}$	298		
Reviews and Evaluations			
$5.4 \times 10^{-12} \exp(-220/T)$	240–400	CODATA, 1984[2]	(b)
$5.4 \times 10^{-12} \exp(-220/T)$	200–300	NASA, 1985[3]	(b)
$5.4 \times 10^{12} \exp(-220/T)$	299–300	NASA, 1987[4]	(b)

Comments

(a) Revised calculations of the measurements of Ogryzlo *et al.*[5]

(b) Based on data of Ogryzlo *et al.*[5]

Preferred Values

$k = 2.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.1 \times 10^{-12} \exp(-210/T)$ cm^3 molecule^{-1} s^{-1} over the range 240–400 K.

Reliability

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

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

Comments on Preferred Value

The slight change from the previous evaluation[2] takes account of the revised calculations[1] on the data of Ogryzlo *et al.*,[5] which result from a correction for the pressure drop along the flow tube between the reaction vessel and the manometer.

References

[1] R. Paltenghi, E.A. Ogryzlo, and K.D. Bayes, J. Phys. Chem. **88**, 2595 (1984).
[2] CODATA Supplement II, 1984 (See References in Introduction).
[3] NASA Evaluation No. 7, 1985 (See References in Introduction).
[4] NASA Evaluation No. 8, 1987 (See References in Introduction).
[5] E.A. Ogryzlo, R. Paltenghi, and K.D. Bayes, Int. J. Chem. Kinet. **13**, 667 (1981).

$CH_3O + NO + M \rightarrow CH_3ONO + M$

$\Delta H^\circ = -173.2$ kJ mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
3×10^{-28}[He]	298	Zellner, 1987[1]	(a)

Comments

(a) Laser photolysis of CH_3ONO at 248 or 351 nm in presence of NO. k determined from rate of recovery of CH_3ONO by time-resolved laser absorption at 257 nm. Falloff curve measured over the range 3.8–375 Torr. k_0 extrapolated using $F_c = 0.6$.

Preferred Values

$k_0 = 3\times10^{-28}$ [He] cm^3 molecule^{-1} s^{-1} at 298 K.

$k_0 = 6\times10^{-28}$ $[N_2]$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_0 = \pm 0.5$

Comments on Preferred Values

The k_0 value for N_2 is estimated using typical relative collision efficiencies of N_2 and He. The large error limit accounts for the fact that there is so far only a single falloff study.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.4×0^{-11}	298	Zellner, 1987[1]	(a)
Reviews and Evaluations			
2×10^{-11}	200–400	CODATA, 1982[2]	(b)
3×10^{-11}	300–400	Atkinson and Lloyd, 1984[3]	(c)

Comments

(a) See comment (a) for k_0

(b) Based on study by Sanders *et al.*[4]

(c) Comparison of $RONO + M \rightarrow RO + NO + M$ dissociation data. Conversion with the equilibrium constants leads to a constant value of k_∞ or $RO + NO + M$ $RONO + M$, independent of R up to C_5.

Preferred Values

$k_\infty = 2x10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the range 200–400 K.

Comments on Preferred Values

The new measurement within the error limits agrees with the earlier results. The preferred unchanged value is a compromise between Refs. 1–4.

Intermediate Falloff Range

The k_0 and k_∞ values from Ref. 1 were obtained with $F_c = 0.6$. The discrepancy in the k_∞ values between Refs. 1, 3, and 4 may point to the need of a smaller F_c value.

References

[1]R. Zellner, J. Chim. Physique **84**, 403 (1987).

[2]CODATA Supplement I, 1982 (See References in Introduction).

[3]N. Sanders, J. E. Butler, R. E. Pasternack, and J. R. McDonald, Chem. Phys. Lett. **48**, 203 (1980).

[4]R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).

$RO + NO + M \rightarrow RONO + M$ (1)

$RO + NO \rightarrow R'O + HNO$ (2)

with $R = C_2H_5$, n-C_3H_7, and i-C_3H_7

Comments

Reaction (1) for $R = i$-C_3H_7 was studied recently[1] by pulsed laser photolysis at 355 nm of i-C_3H_7ONO in the presence of NO. i-C_3H_7O was detected by LIF. Experiments were performed over the range 298–383 K. No variation of $k_1 = 1.2\times10^{-11} \exp(310/T)$ cm^3 molecule^{-1} s^{-1} [corresponding to $k_1(298\ K) = 3.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1}] was observed over the pressure range 1–50 Torr. The small negative temperature coefficient may be attributed to falloff effects; see the results for $R = CH_3$ in this evaluation. The results from Ref. 1 may be considered as representative for other R, in agreement with the evaluation from Ref. 2, which was based on rates of the reverse dissociations of RONO and a conversion via the equilibrium constant. The evaluation from Ref. 2 recommends $k_{1\infty} = 3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 300–400 K. Branching ratios $k_2/(k_1 + k_2) \gtrsim 0.18$ were generally found and assumed to be independent of temperature[2].

References

[1]R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **99**, 323 (1985).

[2]R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).

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

$\Delta H^\circ(1) = -170.5$ kJ mol^{-1}
$\Delta H^\circ(2) = -238.9$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data ($k = k_1$)

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.6\times10^{-29}(T/300)^{-4.5}$[He]	220–473	McCaulley *et al.*, 1985[1]	(a)

Comments

(a) Study in a discharge flow system over the pressure range 0.6–4 Torr in He. CH_3O produced by IR laser dissociation of $C_6F_5OCH_3$ to yield CH_3, followed by $CH_3 + NO_2 \rightarrow CH_3O + NO$, CH_3O monitored by LIF. 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.

Preferred Values

$k_0 = 2.6\times10^{-29}(T/300)^{-4.5}$[He] over the range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.5$.
$\Delta n = \pm 2$.

Comments on Preferred Values

The derived value for k_0 and its temperature coefficient are in good agreement with theoretical simulations by Patrick and Golden.[2] Since this is the only published direct low-pressure study, we assign large error limits. If the experiments of Ref. 1 do not correspond to the low-pressure limit, the true k_0 would be larger than the given value. At the same time, the derived value of k_2 would have to be decreased (see below).

High-pressure rate coefficients
Rate coefficient data ($k = k_1$)

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
1.2×10^{-11}	298–400	CODATA, 1984[3]	(a)
1.5×10^{-11}	300–400	Atkinson and Lloyd, 1984[4]	(b)

Comments

(a) Average of three earlier determinations in the pressure range 50–500 Torr.

(b) Derived on the basis that $k(RO + NO + M)/k(RO + NO_2 + M) = 2$ independent of temperature and taking $k(RO + NO + M) = 3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} irrespective of R (see this evaluation for RO + NO + M).

Preferred Values

$k_\infty = 1.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 300–400 K

Reliability

$\Delta \log k_\infty = \pm 0.3$.

Comments on Preferred Values

There have not been any systematic studies of the pressure dependence over a sufficiently large range such that neither the limiting k_0 nor k_∞ can be established with certainty. Both values can only be lower limits if falloff curves are broader than assumed.

Intermediate Falloff Range

As long as the falloff curves have not been studied more systematically, we recommend $F_c = 0.4$ such as modeled for $CH_3O_2 + NO_2$ in Ref. 2.

Branching ratios

From the branching ratio determinations[3] $k_2/k_1 < 0.1$ at high pressures, one obtains $k_2 < 1.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. Assuming third-order behavior for reaction (1) at pressures below 4 Torr, in Ref. 1 $k_2(298\text{ K}) = (0.9–2.6)\times10^{-13}$ cm^3 molecule^{-1} s^{-1} was derived from the pressure dependence of $k_1 + k_2$. Curvature of the falloff curve would result in an overestimate of k_2.

Preferred values of k_2

$k_2 < 3\times10^{-13}$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Comments on Preferred Values

See under branching ratio.

References

[1] J. A. McCaulley, S. M. Anderson, J. B. Jeffries, and F. Kaufman, Chem. Phys. Lett. **115**, 180 (1985).

[2]R. Patrick and D. M. Golden, Int. J. Chem. Kinet. **15**, 1189 (1983).
[3]CODATA Supplement II, 1984 (See References in Introduction).
[4]R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).

$RO + NO_2 + M \rightarrow RONO_2 + M$ (1)
$RO + NO_2 \rightarrow R'O + HNO_2$ (2)

with $R = C_2H_5$, n-C_3H_7, and i-C_3H_7

Comments

Reaction (1) for $R = i$-C_3H_7 was studied[1] by pulsed laser photolysis of isopropylnitrite at 355 nm in the presence of NO_2. i-C_3H_7O was detected by LIF. By extrapolation to zero laser power, a rate coefficient $k_1 = 1.5 \times 10^{-11} \exp(250/T)$ cm^3 molecule^{-1} s^{-1} was derived from measurements in the range 295–384 K [k_1(298 K) $= 3.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}]. No pressure dependence was observed over the range 1–10 Torr. A comparative evaluation[2] of the rate coefficients for the reactions $RO + NO_2 + M$ and $RO + NO + M$, on the basis of $k(RO + NO + M)/k(RO + NO_2 + M) = 2 \pm 1$ independent of the temperature, and using $k(RO + NO + M) = 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} leads to $k_1 = 1.5 \times 10^{11}$ cm^3 molecule^{-1} s^{-1} irrespective of R. So far no falloff data are available from direct measurements of reaction (1). However, some information could be inferred from measurements of the reverse pyrolysis such as, e.g., for $R = n$-C_3H_7 in Ref. 3. Reaction (2) appears to be the minor channel[4] ($k_2/k_1 \lesssim 0.2$) in the high pressure range of reaction (1). However, more direct information is required to establish reliable information on the branching ratio.

References

[1]R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **99**, 32 (1985).
[2]R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984)
[3]G. D. Mendenhall, D. M. Golden, and S. W. Benson, Int. J. Chem. Kinet 7, 725 (1975).
[4]K. L. Demerjan, J. A. Kerr, and J. G. Calvert, Adv. Environ. Sci. Technol **4**, 1 (1974).

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

Comments

Zellner, Fritz, and Lorenz have reported a value of $k = (7 \pm 2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K for this reaction from laser-pulsed photolyses experiments, involving mixtures of $(CH_3)_2N_2$–O_2–NO, in which the $[CH_3O_2]$ was monitored by ultraviolet absorption at 257 nm. This result is in excellent agreement with our previous recommendation,[2] which remains unaltered.

In addition Zellner *et al.*[1] and Zellner[3] have carried out product studies, which show that $\phi(CH_3O) = 1.0 \pm 0.2$, confirming that the product channel to give CH_3O and NO_2 is the major, if not the only, reaction pathway.

References

[1]R. Zellner, B. Fritz, and K. Lorenz, J. Atmos. Chem. **4**, 241 (1986).
[2]CODATA Supplement II, 1984 (See References in Introduction).
[3]R. Zellner, J. Chim. Phys. Phys.-Chim. Biol. **84**, 403 (1987).

$RO_2 + NO \rightarrow RO + NO_2$ (1)
$RO_2 + NO + M \rightarrow RONO_2 + M$ (2)

Comments

Atkinson *et al.*[1] have recalculated the branching ratios listed below from their original data,[2] on the basis of revised data for the rate coefficients of the HO + alkane reactions, which are required in the determination:

RO_2	k_2/k(299 K),
$C_2H_5O_2$	$\leqslant 0.014$,
n-$C_3H_7O_2$	0.020 ± 0.009,
i-$C_3H_7O_2$	0.043 ± 0.003.

For the $C_2H_5O_2$ radical the individual values of k_1 and k_2 listed in the Summary have been calculated from the above ratio and our previously recommended value[3] of $k = (k_1 + k_2) = 8.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K. Likewise the values of k_1 and k_2 for n-$C_3H_7O_2$ and i-$C_3H_7O_2$ radicals have been calculated from the above ratios and by assuming that $k = 8.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K for the $C_3H_7O_2$ radicals as well.

References

[1]R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **16**, 1085 (1984).
[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]CODATA Supplement II, 1984 (See References in Introduction).

$CH_3O_2NO_2 + M \rightarrow CH_3O_2 + NO_2 + M$

$\Delta H^\circ = 100$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.3\times10^{-4}\exp(-10140/T)$ [CH_4]	256–268	Bahta, Simonaitis, and Heicklen, 1982[1]	(a)
5.5×10^{-19} [CH_4]	298*		
$9.0\times10^{-5}\exp(-9694/T)$ [N_2]	248–273	Reimer *et al.*, 1988[2]	(b)
6.7×10^{-19} [N_2]	298*		
Reviews and Evaluations			
5.6×10^{-19} [air]	298	NASA, 1987[3]	(c)

Comments

(a) $CH_3O_2NO_2$ generated by photolysis of Cl_2 in the presence of NO_2, CH_4, and O_2. Kinetics monitored in the presence of NO by UV absorption at 250 nm. Pressure range 50–720 Torr of mostly CH_4 (in some cases N_2). k(350 Torr) $= 6\times10^{15}\exp(-10620/T)$ s^{-1}. The given k_0 and k_∞ values are derived using $F_c = 0.6$. The data to some extent depend on the rate coefficient for $CH_3O_2 + NO \rightarrow CH_3O + NO_2$.

(b) Rate of decomposition of $CH_3O_2NO_2$ followed by FTIR after generation in a smog chamber and subsequent addition of NO to scavenge CH_3O_2 radicals. Falloff curves fitted with $F_c = 0.4$, accounting for increasing width using N from Ref. 4.

(c) Converted from the reverse reaction and an equilibrium constant $K = 1.3\times10^{-28}\exp(+11\,200/T)$ cm^3 molecule^{-1} ($200 < T < 300$ K).

Preferred Values

$k_0 = 9\times10^{-5}\exp(-9690/T)[N_2]$ s^{-1} over the range 250–300 K.

$k_0 = 6.8\times10^{-19}[N_2]$ s^{-1} at 298 K.

Reliability

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

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

Comments on Preferred Values

The preferred value from Ref. 2 appears consistent with the data from Ref. 1, which were evaluated using a larger $F_c = 0.6$. The value from Ref. 3 is also slightly lower since $F_c = 0.6$ was used in order to represent the falloff results for the reverse reaction. The different representations all reproduce the measured part of the falloff curve equally well, if the equilibrium constant $K = 1.3\times10^{-28}\exp(+11\,200/T)$ cm^3 molecule^{-1} from Ref. 3 is used for a conversion.

High-pressure rate coefficients
Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.1\times10^{16}\exp(-10\,920/T)$	256–268	Bahta, Simonaitis, and Heicklen, 1982[1]	(a)
2.6	298*		
$1.1\times10^{16}\exp(-10\,560/T)$	248–273	Reimer *et al.*, 1988[2]	(b)
4.5	298*		
Reviews and Evaluations			
2.4	298	NASA, 1987[3]	(c)

Comments

(a) See comment (a) for k_0.
(b) See comment (b) for k_0.
(c) See comment (c) for k_0.

Preferred Values

$k_\infty = 1.1\times10^{16}\exp(-10560/T)$ s^{-1} over the range 250–300 K.

$k_\infty = 4.5$ s^{-1} at 298 K.

Reliability

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

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

Comments on Preferred Values

See comment on preferred value of k_0.

Intermediate Falloff Range

The preferred k_0 and k_∞ values were obtained using $F_c = 0.4$.

References

[1]A. Bahta, R. Simonaitis, and J. Heicklen, J. Phys. Chem. **86**, 1849 (1982).
[2]A. Reimer, K. H. Becker, E. H. Fink, and F. Zabel (to be published).
[3]NASA Evaluation No. 8, 1987 (See References in Introduction).
[4]J. Troe, J. Phys. Chem. **83**, 114 (1979).

$C_2H_5O_2NO_2 + M \rightarrow C_2H_5O_2 + NO_2 + M$

Comments

In a recent experimental study, Reimer *et al.*[1] measured the thermal decomposition of $C_2H_5O_2NO_2$ by long path FTIR (see technique described in comment (a) for $CH_3O_2NO_2 + M \rightarrow CH_3O_2 + NO_2 + M$ of this evaluation). The following rate coefficients were obtained over the temperature range 245–265 K: $k = 4.7\times10^{15}\exp(-10370/T)$ s^{-1} at 800 mbar of N_2, $k = 7.9\times10^{13}\exp(-9660/T)$ s^{-1} at 10.4 mbar of N_2. A falloff extrapolation using $F_c = 0.2$ and the corresponding $N = 1.64$ from Ref. 2, at 253 K leads to $k_0 = 1.1\times10^{-19}[N_2]$ s^{-1} and $k_\infty = 1.3\times10^{-2}$ s^{-1}. These data are in accord with estimates by Atkinson and Lloyd[3] based on studies of related reactions. A more detailed representation of the data from Ref. 1 will appear soon.

References

[1]A. Reimer, K. H. Becker, E. H. Fink, and F. Zabel (to be published).
[2]J. Troe, J. Phys. Chem. **83**, 114 (1979).
[3]R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).

$CH_3CO_3 + NO_2 + M \rightarrow CH_3CO_3NO_2 + M$

Low-pressure rate coefficient
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.1\times10^{-29}[N_2]$	298	Basco and Parmar, 1987[1]	(a)

Comments

(a) Flash photolysis with detection of CH_3CO_3 via absorption at 250 nm. Mixtures of Cl_2, CH_3CHO, O_2, N_2, and NO_2 photolyzed at total pressures of 76–612 Torr. Extrapolation of falloff curve with theoretically modeled value of $F_c = 0.19$.

Preferred Values

$k_0 = 2\times10^{-28}[N_2]$ cm^3 molecule^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

Using the data from Ref. 1 and a value of the equilibrium constant K_c(298 K) $= 1.4\times10^{-8}$ cm^3 molecule^{-1} from the ratio of forward and backward rates near the high-pressure limit (this evaluation), a rate coefficient for the reverse reaction $CH_3CO_3NO_2 + M \rightarrow CH_3CO_3 + NO_2 + M$ of $k_0(298\text{ K}) = 3.6\times10^{-21}[N_2]$ s^{-1} would be obtained that is about a factor of 4 smaller than the recent value from Ref. 2. Since the data from Ref. 2 show much less scatter, their falloff extrapolation is probably more reliable and is preferred here.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
6.1×10^{-12}	298	Basco and Parmar, 1987[1]	(a)
Reviews and Evaluations			
6×10^{-12} (1 atm air)	298	CODATA, 1984[3]	(b)
9.3×10^{-12} (1 atm air)	298	Atkinson and and Lloyd, 1984[4]	(c)

Comments

(a) See comment for k_0.

(b) Based on data of Addison *et al.*[5]

(c) Calculated from recommendation that $k(CH_3CO_3 + NO)/k(CH_3CO_3 + NO_2) = 1.5$ at 1 atm and taking $k(CH_3CO_3 + NO) = 1.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K (CODATA evaluation).

Preferred Values

$k_\infty = 8.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

Preferred value from Refs. 1 and 5 using a falloff correction from k (1 atm) to k_∞ of a factor of 1.4. The falloff extrapolation to k_∞ appears fairly straight-forward whereas k_0 is more difficult to obtain.

Intermediate Falloff Range

An F_c value of 0.27 is recommended as for the reverse reaction, since k_0 and k_∞ are in part based on results from the reverse reaction.

References

[1] N. Basco and S. S. Parmar, Int. J. Chem. Kin. **19**, 115 (1987).
[2] A. Reimer, K. H. Becker, E. H. Fink, and F. Zabel (to be published).
[3] CODATA Supplement II, 1984 (See References in Introduction).
[4] R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).
[5] M. C. Addison, J. P. Burrows, R. A. Cox, and R. Patrick, Chem. Phys. Lett. **73**, 283 (1980).

$CH_3CO_3NO_2 + M \rightarrow CH_3CO_3 + NO_2 + M$

Low-pressure rate coefficients
Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.3 \times 10^{-2} \exp(-12785/T)[N_2]$	302–321	Reimer *et al.*, 1988[1]	(a)
$1.5 \times 10^{-20}[N2]$	298*		

Comments

(a) Rate of the thermal decomposition of PAN, in an excess of NO to scavenge CH_3CO_3, measured in a smog chamber by FTIR absorption. Pressure range 7.5–600 Torr of N_2. Falloff curves analyzed with $F_c = 0.27$ and the corresponding $N = 1.47$ from Ref. 2.

Preferred Values

$k_0 = 6.3 \times 10^{-2} \exp(-12785/T)[N_2]$ s^{-1} over the range 300–320 K.

$k_0 = 1.5 \times 10^{-20}[N_2]$ s^{-1} at 298 K.

Reliability

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

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

Comments on Preferred Values

Since the extrapolation of the data from Ref. 1 to the low pressure limit is fairly far, large error limits are assigned.

High-pressure rate coefficients
Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.3 \pm 0.2) \times 10^{-4}$ (700 Torr N_2)	297	Niki *et al.*, 1985[3]	(a)
2.2×10^{-4} (12.4 Torr NO)	298	Senum, Fajer, and Gaffney, 1986[4]	(b)
$2.2 \times 10^{-16} \exp(-13\,435/T)$	302–321	Reimer *et al.*, 1988[1]	(c)
5.8×10^{-4}	298*		
Reviews and Evaluations			
$1.12 \times 10^{16} \exp(-13\,330/T)$ (1 atm)	295–330	CODATA, 1984[5]	(d)
4.2×10^{-4}	298		
$2 \times 10^{16} \exp(-13\,510/T)$ (1 atm)	298–313	Atkinson and Lloyd, 1984[6]	(e)
4.1×10^{-4}	298		

Comments

(a) Decay of $CH_3CO_3{}^{15}NO_2$ in presence of $^{14}NO_2$ monitored by FTIR spectroscopy in a long-path cell at total pressure of 700 Torr.

(b) Decay of $CH_3CO_3NO_2$ (2 Torr) in presence of NO (0.2–10.3 Torr) monitored by FTIR spectroscopy in a 10 cm cell. Second channel, leading to $CH_3ONO_2 + CO_2$, monitored via CH_3ONO_2–FTIR absorption (experiments with

2.4 to 27.5 Torr of pure PAN and no added gases). The rate coefficient derived $k(298\ \mathrm{K}) = 1.3\times10^{-6}\ \mathrm{s}^{-1}$, and the evidence for this channel needs to be confirmed.

(c) See Comment for k_0.

(d) Based on data from Refs. 7–10.

(e) Based on data from Ref. 10.

Preferred Values

$k_\infty = 2.2\times10^{16} \exp(-13\,435/T)\ \mathrm{s}^{-1}$ over the range 300–320 K.

$k_\infty = 5.8\times10^{-4}\ \mathrm{s}^{-1}$ at 298 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are from Ref. 1. They are somewhat larger than the earlier data for k_∞ because the falloff effects at 1 atm are taken into account. The actual rate coefficients at 1 atm from the various studies agree remarkably well.

Intermediate Falloff Range

The preferred k_0- and k_∞-values were obtained using $F_c = 0.27$. A theoretical estimate of $F_c = 0.19$ was estimated in Ref. 11 for the reverse reaction (see this evaluation).

References

[1] A. Reimer, K. H. Becker, E. H. Fink, and F. Zabel, (to be published).
[2] J. Troe, J. Phys. Chem. **83**, 114 (1979).
[3] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **17**, 525 (1985).
[4] G. I. Senum, R. Fajer, and J. S. Gaffney, J. Phys. Chem. **90**, 152 (1986).
[5] CODATA Supplement I, 1982 (See References in Introduction).
[6] R. Atkinson and A. C. Lloyd J. Phys. Chem. Ref. Data **13**, 315 (1984).
[7] C. T. Pate, R. Atkinson and J. N. Pitts, J. Environ. Sci. Health–Environ. Sci. Eng. **A11**, 19 (1976).
[8] R. A. Cox and J. J. Roffey, Environ. Sci. Technol. **11**, 900 (1977).
[9] D. G. Hendrey and R. A. Kenley, J. Am. Chem. Soc. **99**, 3198 (1977).
[10] U. Schurath and V. Wipprecht, First European Symposium on Physicochemical Behavior of Atmospheric Pollutants, Ispra, Italy, 1979.
[11] N. Basco and S. S. Parmar, Int. J. Chem. Kinet. **19**, 115 (1987).

$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2$ (1)
$\rightarrow 2CH_3O + O_2$ (2)
$\rightarrow CH_3OOCH_3 + O_2$ (3)

$\Delta H^\circ(1) = -355.7\ \mathrm{kJ\ mol^{-1}}$
$\Delta H^\circ(2) = -10.8\ \mathrm{kJ\ mol^{-1}}$
$\Delta H^\circ(3) = -171.5\ \mathrm{kJ\ mol^{-1}}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.2\pm1.5)\times10^{-13}$	298	Basco and Parmar, 1985[1]	(a) (b)
$(4.4\pm1.0)\times10^{-13}$	298	McAdam, Veyret, and Lesclaux, 1987[2]	(a) (c)
$(1.3\pm0.3)\times10^{-13}\exp[(220\pm70/T)]$	228–380	Kurylo and Wallington, 1987[3]	(a) (d)
$(2.7\pm0.45)\times10^{-13}$	298		
$(3.5\pm0.5)\times10^{-13}$	298	Jenkin *et al.*, 1988[4]	(a) (e)
Reviews and Evaluations			
3.7×10^{-13}	298	CODATA, 1984[5]	(f)
$1.6\times10^{-13}\exp(+220/T)$	200–300	NASA, 1985[6]	(g)
$1.9\times10^{-13}\exp(+220/T)$	200–300	NASA, 1987[7]	(h)

Comments

(a) k is defined by $-d[CH_3O_2]/dt = 2k[CH_3O_2]^2$ and has been derived from the measured overall second-order decay of CH_3O_2 (k_0) by correcting for secondary removal of CH_3O_2.

(b) Flash photolysis of Cl_2 in the presence of CH_3CHO and O_2 at total pressures of 153 Torr. $[CH_3O_2]$ monitored by absorption spectroscopy at long delay times after the flash, such that $[CH_3O_2] \gg [CH_3CO_3]$. k_0/σ values were not reported. k has been calculated from the measured value of $k_0 = 7.0\times10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ and taking $k_0/k = 1.35$.

(c) Flash photolysis of Cl_2 in the presence of CH_4 and O_2 over the pressure range 120–400 Torr. $[CH_3O_2]$ monitored by UV absorption. $k_0/\sigma\ (250\ \mathrm{nm}) = 1.34\times10^5\ \mathrm{cm\ s^{-1}}$ and $\sigma(250\ \mathrm{nm}) = 4.4\times10^{-18}\ \mathrm{cm^2\ molecule^{-1}}$. k_0/k taken to be 1.35

(d) Flash photolysis of Cl_2 in presence of CH_4–O_2–N_2 mixtures at pressures between 50 and 400 Torr. $[CH_3O_2]$ monitored by absorption at 250 nm; $k_0 = (1.7\pm0.4)\times10^{-13}\exp[(220\pm70)/T]\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ determined from measured values of k_0/σ (250) by taking $\sigma(250) = 3.30\times10^{-18}\ \mathrm{cm^2}$ as previously determined by same authors. Here we have taken $k_0/k = 1.35$ to calculate k. k_0 shown to be independent of pressure (50–400 Torr) at 298 K.

(e) Molecular modulation spectrometry, CH_3O_2 generated by photolysis of Cl_2 in the presence of CH_4–O_2 mixtures at a total pressure of 760 Torr. CH_3O_2 monitored by absorption over range 210–270 nm. k_0/σ (250) $= 1.11 \times 10^5$ cm s^{-1} and σ(250 nm) $= (4.25 \pm 0.5) \times 10^{-18}$ cm^2 molecule^{-1} leading to $k_0 = (4.7 \pm 0.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Above value of k obtained by taking $k_0/k = 1.35$ to allow for secondary removal of CH_3O_2.

(f) Based on data of Kan and Calvert,[8] Sanhueza *et al.*,[8] Kan *et al.*[10] Cox and Tyndall,[11] Sander and Watson,[12] Adachi *et al.*,[13] Hochanadel *et al.*,[14] and Parks.[15]

(g) Based on data of Hochanadel *et al.*,[14] Parkes,[15] Anastasi *et al.*,[16] Sanhueza *et al.*,[9] and Sander and Watson.[12]

(h) As for comment (g) plus data of McAdams *et al.*[2]

Preferred Values

$k = 3.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.7 \times 10^{-13} \exp(+220/T)$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

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

Reliability

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

$\Delta (E/R) = \pm 220$ K.

$\Delta (k_2/k) = \pm 0.15$ K.

$\Delta (k_3/k) = \pm 0.08$ K.

Comments on Preferred Values

There is good agreement among the values of k_0/σ, which have been reported for this reaction. We have derived the preferred value of k_{298} from the average value of k_0/σ (250 nm) $= 1.24 \times 10^5$ cm s^{-1} based on the results of Parkes,[16] Hochanadel *et al.*,[15] Anastasi *et al.*,[17] Kan *et al.*,[14] Adachi *et al.*,[13] Sander and Watson,[12] McAdam *et al.*,[2] Kurylo *et al.*,[3] and Jenkin *et al.*[4] It appears that k_0/σ (250 nm) is independent of pressure over the range 50 to 760 Torr.

The value $k_0 = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K was then obtained by taking $\sigma(250 \text{ nm}) = 3.9 \times 10^{-18}$ cm^2 molecule^{-1}, which is an average value derived from the data of McAdam *et al.*,[2] Kurylo and Wallington,[3] Jenkin *et al.*,[4] Kan *et al.*,[10] Cox and Tyndall,[11] Sander and Watson,[12] Adachi *et al.*,[13] Hochanadel *et al.*,[14] Parkes,[15] Anastasi *et al.*,[16] Moortgat *et al.*,[17] and Pilling and Smith.[18]

The correction of k_0 to k, to allow for the secondary removal of CH_3O_2 radicals arising from the reactions of the product CH_3O radicals from channel (2), is based on the branching ratio $k_2/k = 0.35$, which was recommended in our previous evaluation[5] and remains unaltered here. It has been pointed out by Jenkin *et al.*[4] that the branching ratios could vary with pressure, in which case the elementary rate coefficient ($k = k_1 + k_2 + k_3$) would possess a pressure dependence which is not apparent in the observed rate coefficient ($k_0 = k_1 + 2k_2 + k_3$).

The temperature dependence of k reported by Kurylo *et al.*[3] agrees with the earlier measurements of Sanders and Watson and is recommended here.

Further studies are required to establish the pressure and temperature dependencies of the branching ratios of this reaction.

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$CH_3O_2 + CH_3CO_3 \rightarrow CH_3O + CH_3CO_2 + O_2$ (1)
$\rightarrow CH_3CO_2H + HCHO + O_2$ (2)

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

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
3×10^{-12}	302	Addison *et al.* 1980[1]	(a)
$(1.4 \pm 0.3) \times 10^{-11}$	253–368	Moortgat, Veyret, and Lesclaux, 1988[2]	(b)
$k_1 = 1.8 \pm \times 10^{-9} \exp[-(1800 \pm 1100)/T]$	253–368		
$k_1 = (5.5 \pm 3) \times 10^{-12}$	298		
$k_2 = 4.1 \times 10^{-15} \exp[(2100 \pm 1200)/T]$	253–368		
$k_2 = (5.5 \pm 2) \times 10^{-12}$	298		

Comments

(a) Molecular modulation study involving UV absorption of CH_3CO_3 (210–280 nm) produced from the photolysis of Cl_2 in the presence of CH_3CHO–O_2 mixtures at a total pressure of 710 Torr. k obtained from a computer simulation of absorption curves, involving a mechanism of nine elementary reactions.

(b) Flash photolysis of Cl_2 in the presence of CH_3CHO–O_2 mixtures at a total pressure of 620 Torr. Rate coefficients derived by fitting the experimental optical density traces at several wavelengths in the range 200–250 nm using a computer simulation model of CH_3O_2 and CH_3CO_3 reactions together with the absorption cross-sections of the radicals. Inclusion of channel (2) was necessary to account for the observed removal of CH_3O_2 in the first 100 μs after the flash.

Preferred Values

$k_1 = 5.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 5.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_1 = \pm 0.5$ at 298 K.
$\Delta \log k_2 = \pm 0.5$ at 298 K.

Comments on Preferred Values

The two reported studies of this reaction are not in good agreement. The discrepancy arises primarily from the different absorption cross sections used for the CH_3CO_3 radical and the rate coefficient determined for its self-reaction in these studies. We have selected the more recent study of Moortgat *et al.*[2] as the basis for a recommendation, on the grounds that the CH_3CO_3 cross-section determination is more direct, and the complex kinetic behavior of the radicals appears to be better defined in the flash photolysis system. Further confirmation of the rate and the branching ratio of this reaction are required.

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$$\begin{aligned} C_2H_5O_2 + C_2H_5O_2 &\rightarrow C_2H_5OH + CH_3CHO + O_2 && (1)\\ &\rightarrow 2C_2H_5O + O_2 && (2)\\ &\rightarrow C_2H_5OOC_2H_5 + O_2 && (3)\end{aligned}$$

$\Delta H^\circ(1) = -387$ kJ mol^{-1}
$\Delta H^\circ(2) = -19.4$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.2\pm0.5)\times10^{-13}\exp[-(517\pm36)/T]$	303–457	Anastasi, Waddington, and Woolley, 1983[1]	(a) (b)
9.2×10^{-14}	298*		
$k_1 = 3.0\times10^{-14}\exp(-109/T)$	302–373		(b)
$k_1 = 2.1\times10^{-14}$	298*		
$k_2 = 3.09\times10^{-13}\exp(-643/T)$	302–373		(b)
$k_2 = 3.5\times10^{-14}$	298*		
3.3×10^{-14}	298	Munk *et al.*, 1986[2]	(a) (c)
8.1×10^{-14}	266–348	Cattell *et al.*, 1986[3]	(a) (d)
$(8.5\pm1.1)\times10^{-14}\exp[-(110\pm40)/T]$	228–380	Wallington, Dagaut, and Kurylo, 1988[4]	(a) (e)
5.9×10^{-14}	298		
Branching Ratios			
$k_2/k_1 = 10.3\exp(-530/T)$	302–373	Anastasi, Waddington, and Woolley, 1983[1]	(b)
$k_2/k_1 = 1.7$	298*		
Reviews and Evaluations			
1×10^{-13}	298	CODATA, 1984[5]	(f)

Comments

(a) k is defined by $-d[C_2H_5O_2]/dt = 2k[C_2H_5O_2]^2$ and has been derived from the measured overall second-order decay of $C_2H_5O_2$ (k_0) by correcting for secondary removal of $C_2H_5O_2$.

(b) Molecular modulation study. $C_2H_5O_2$ determined by absorption at 240 nm from photolysis of $(C_2H_5)_2N_2$ in the presence of O_2 (5–150 Torr) and N_2 (410–550 Torr). k/σ (240) and $\sigma(240)$ found to be temperature dependent. k_1 and k_2 obtained from k_0 and branching ratio, k_2/k_1, determined from analysis of products C_2H_5OH and CH_3CHO by gcms. Calculation of k_1 and k_2 allows for secondary removal of $C_2H_5O_2$ by reaction of products from channel (2). Note that the temperature dependencies of k_1 and k_2 listed above differ from those listed in the paper, which are in error.[6]

(c) Pulse radiolysis of H_2 (1 atm) in present of C_2H_4 to generate C_2H_5 from $H + C_2H_4$. $C_2H_5O_2$ observed in the presence of O_2. $k_0 = 5.23\times10^{-14}$ cm^3 molecule^{-1} s^{-1} obtained from measured decay of $C_2H_5O_2$ determined by adsorption at 240 nm. k calculated on the assumption that $k_0/k = 1.6$. From experimental value of σ(240 nm) $= 5.20\times10^{-18}$ cm^2 molecule^{-1} this corresponds to $k_0/\sigma(240) = 1.0\times10^4$ cm s^{-1}.

(d) Molecular modulation spectroscopy. $C_2H_5O_2$ generated from photolysis of Cl_2 in presence of C_2H_6–O_2–N_2 mixtures at pressures between 2.4 and 760 Torr and monitored by absorption at 260 nm. Over the temperature range quoted $k_0/\sigma(260) = (4.07\pm0.44)\times10^4$ cm s^{-1} and σ(260 nm) $= (3.20\pm0.38)\times10^{-18}$ cm^2 molecule^{-1} leading to $k_0 = (1.30\pm0.16)\times10^{-13}$ cm^3 molecule^{-1} s^{-1}. Above value of k obtained by taking $k_0/k = 1.6$, to allow for secondary removal of $C_2H_5O_2$.

(e) Flash photolysis of Cl_2 in the presence of C_2H_6–O_2–N_2 mixtures at total pressures of 25–400 Torr. Absorption cross sections of $C_2H_5O_2$ were measured over the range 215–300 nm with σ(250 nm) $= (3.89\pm0.54)\times10^{-18}$ cm^2 molecule^{-1}. At 298 K $k_0/\sigma = 2.53\times10^4$ cm s^{-1} and over range 228–380 K, $k_0 = (1.41\pm0.19)\times10^{-13}\exp[-(110\pm40)/T]$ cm^3 molecule^{-1} s^{-1} measured at a total pressure of 100 Torr and based on σ(250 nm). Above value of k was calculated from k_0 by Dagaut, Wallington, and Kurylo on the basis of their data for $k(HO_2 + C_2H_5O_2)$.

(f) Based on data of Adachi *et al.*[8]

Preferred Values

$k = 8.6\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.2\times10^{-13}\exp(-110/T)$ cm^3 molecule^{-1} s^{-1} over range 250–450 K.

$k_2/k = 0.60$ at 298 K.

Reliability

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

$\Delta (E/R) = {}^{+300}_{-100}$ K.

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

Comments on Preferred Values

The preferred value of k_{298} is the mean of the data of Adachi *et al.*,[8] Anastasi *et al.*,[1] Cattell *et al.*,[3] and Wallington *et al.*[4] It is not possible to compare directly the measured values of k_0/σ in these studies since the experiments involved several different wavelengths.

The consensus of evidence suggests that the rate coefficient has a small positive temperature coefficient, and we have selected the measurements of Wallington *et al.*[4] as a basis for our recommendation.

The recommended branching ratio k_2/k has been calculated from the mean value of k_1/k_2, taken from Niki *et al.*[9] ($k_1/k_2 = 0.76$ at 298 K) and from Anastasi *et al.*[1] ($k_1/k_2 = 0.59$ at 298 K). The temperature dependencies of the branching ratio reported by Anastasi *et al.*[1] require confirmation.

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$n\text{-}C_3H_7O_2 + n\text{-}C_3H_7O_2 \rightarrow n\text{-}C_3H_7OH + C_2H_5CHO + O_2$ (1)

$\rightarrow 2n\text{-}C_3H_7O + O_2$ (2)

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.3\pm0.3)\times10^{-13}$	298	Adachi and Basco, 1982[1]	(a) (b)

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 $n\text{-}C_3H_7O_2$ (k_0) by correcting for secondary removal of $n\text{-}C_3H_7O_2$.

(b) Flash photolysis of 1,1′-azopropane in the presence of O_2 and added N_2 at total pressures upto 720 Torr. $[n\text{-}C_3H_7O_2]$ monitored by absorption at 260 nm for which $\sigma(260\,\text{nm}) = 3.15\times10^{-18}$ cm^3 molecule^{-1} s^{-1}. k calculated from experimental $k_0 = (3.84\pm0.33)\times10^{-13}$ on the basis of a mechanism of 12 elementary reactions, including secondary removal of $n\text{-}C_3H_7O_2$ radicals.

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, which is the rounded-off value from the study of Adachi and Basco,[1] 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 interaction of the i-$C_3H_7O_2$ radical is considerably lower ($k_{298} = 1.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}) and that reported[2] for the t-$C_4H_9O_2$ 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 interactions,[3] i.e., $k(\text{primary RO}_2) > k(\text{secondary RO}_2) > k(\text{tertiary RO}_2)$.

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i-$C_3H_7O_2$ + i-$C_3H_7O_2$ → i-C_3H_7OH + $(CH_3)_2CO$ + O_2 (1)

→ 2i-C_3H_7O + O_2 (2)

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.43 \pm 0.10) \times 10^{-12} \exp[-(2243 \pm 69)/T]$	300–373	Kirsch *et al.*, 1978[1]	(a) (b)
8.10×10^{-16}	300		
$(1.3 \pm 0.4) \times 10^{-15}$	298	Adachi and Basco, 1982[2]	(a) (c)
$(5.3 \pm 0.5) \times 10^{-14}$	298	Munk *et al.*, 1986[3]	(a) (d)
Branching Ratios			
$k_2/k_1 = 1.39 \pm 0.04$	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)

Comments

(a) k is defined by $-d[i\text{-}C_3H_7O_2]/dt = 2k[i\text{-}C_3H_7O_2]$ and has been derived from the measured overall second-order decay of i-$C_3H_7O_2$ (k_0) by correcting for secondary removal of i-$C_3H_7O_2$.

(b) Molecular modulation study of the photolysis of 2,2′-azopropane in the presence of O_2 and N_2 at pressures upto 710 Torr. $[i\text{-}C_3H_7O_2]$ monitored by absorption at 265 nm. k has been calculated from the experimental value of $k_0 = (2.37 \pm 0.17) \times 10^{-12} \exp[-(2243 \pm 60)/T]$ cm^3 molecule^{-1} s^{-1} and the branching ratio $k_2/k_1 = 1.39$ at 302 K determined in a subsequent study.

(c) Flash photolysis of 2,2′-azopropane in the presence of O_2 and added N_2 at total pressures upto 720 Torr. $[i\text{-}C_3H_7O_2]$ monitored by absorption at 240 nm for which $k_0(240\,\text{nm}) = 4.86 \times 10^{-18}$ cm^2 molecule^{-1}. k has been calculated from the experimental value of $k_0 = (2.03 \pm 0.58) \times 10^{-15}$ 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-$C_3H_7O_2$ radicals.

(d) Pulse radiolysis of H_2 at 1 atm in presence of C_3H_6. i-C_3H_7 generated from H + C_3H_6 and monitored by UV absorption at 253 nm. Absorption spectrum of i-$C_3H_7O_2$ observed on addition of O_2 and decay of i-$C_3H_7O_2$, found to obey second-order kinetics. It is not clear if reported value of rate coefficient is k_0 or k, but we have assumed that it is k.

(e) Steady-state photolysis of 2,2′-azopropane in the presence of O_2 and added N_2 at total pressures upto 500 Torr. Ratio of rate coefficients based on analyses of $(CH_3)_2CO$ and $(CH_3)_2CHOH$ by gas chromatography.

(f) Extension of the experiments by Kirsch *et al.*[4] to obtain k_2/k_1 at 333 and 372 K. Arrhenius equation calculated from these data and value of k_2/k_1 at 302 K reported by Kirsch *et al.*[4]

Preferred Values

$k = 1.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.6 \times 10^{-12} \exp(-2200/T)$ cm^3 molecule^{-1} s^{-1} over the range 300–400 K.

$k_1/k = 0.44$ at 298 K.

$k_1/k = 3.7 \times 10^{-2} \exp(740/T)$ over the range 300–400 K.

$k_2/k = 0.56$ at 298 K.

$k_2/k = 2.0 \exp(-380/T)$ over the range 300–400 K.

Reliability

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

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

$\Delta (k_1/k) = \Delta (k_2/k) = \pm 0.15$ 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.*[1,4] and from 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 branching ratio and its temperature dependence[4,5] appear to be reliable and have been adopted here but require further confirmation.

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, i.e., $k(\text{primary } RO_2) > k(\text{secondary } RO_2) > k(\text{tertiary } RO_2)$.

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$CH_3CO_3 + CH_3CO_3 \rightarrow 2CH_3CO_2 + O_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.5^{+2.5}_{-1.3})\times10^{-12}$	302	Addison *et al.*, 1980[1]	(a) (b)
$(8.0\pm1.3)\times10^{-12}$	298	Basco and Parmar, 1985[2]	(a) (c)
$(2.8\pm0.5)\times10^{-12}\exp[(530\pm100)/T]$	253–368	Moortgat, Veyret, and Lesclaux, 1989[3]	(a) (d)
$(1.6\pm0.3)\times10^{-11}$	298		

Comments

(a) k is defined by $-d[CH_3CO_3]/dt = 2k[CH_3CO_3]^2$ and has been derived from the measured overall second-order decay of CH_3CO_3 (k_0) by correcting for secondary removal of CH_3CO_3.

(b) Molecular modulation study involving UV absorption of CH_3CO_3 (210–280 nm) produced from the photolysis of Cl_2 in the presence of CH_3CHO and O_2 at total pressures of 710 Torr. A computer simulation of the absorption curves, involving a mechanism of nine elementary reactions with secondary removal of CH_3CO_3 yields the quoted value of k from the experimental value of $k_0 = (6.5\pm3.0)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(c) Flash photolysis of Cl_2 in the presence of CH_3CHO and O_2 at a total pressure of 153 Torr. CH_3CO_3 monitored by UV absorption (210–218 nm). k derived from a computer simulation of absorption profiles over wavelength range 198–208 nm where the CH_3O_2 contribution to the total absorbance was assumed to be negligible. Reported rate coefficient, which is listed above, is effectively k.

(d) Flash photolysis of Cl_2 in presence of CH_3CHO–O_2 mixtures at a total pressure of 620 Torr. $[CH_3CO_3]$ monitored by absorption over range 190–280 nm and absorption cross section measured relative to $\sigma(HO_2) = 5.3\times10^{-18}$ cm^3 molecule^{-1} at 210 nm. Rate coefficient derived from a computer simulation from a mechanism, including secondary removal of CH_3CO_3, of the absorption traces at a range of wavelengths.

Preferred Values

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

$k = 2.8\times10^{-12}\exp(530/T)$ cm^3 molecule^{-1} s^{-1} over range 250–370 K.

Reliability

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

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

Comments on Preferred Values

The agreement among the three measurements[1-3] of this rate coefficient at room temperature is rather poor. We have selected the most recent study of Moortgat *et al.*[3] as the basis for a recommendation, on the grounds that it is based upon a more complete knowledge of the complicated chemistry involved than was available for the earlier studies.[1,2] At the same time, until more experimental data are available we have assigned considerable error limits, particularly with regard to the temperature coefficient.

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$RCHOO + O_3 \rightarrow RCHO + 2O_2$ (1)
$RCHOO + H_2O \rightarrow RCOOH + H_2O$.(2)
$RCHOO + CO \rightarrow$ products (3)
$RCHOO + HCHO \rightarrow RCHOOCH_2O$ (4)
$RCHOO + C_2H_4 \rightarrow$ products (5)
$RCHOO + NO \rightarrow RCHO + NO_2$ (6)
$RCHOO + NO_2 \rightarrow RCHO + NO_3$ (7)
$RCHOO + SO_2 \rightarrow$ products (8)
($R = H$ or CH_3)

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$k_2/k_8 = (6.1 \pm 0.3) \times 10^{-5}$	295	Calvert *et al*, 1978[1]	(a)
$k_1{:}k_3{:}k_4{:}k_5{:}k_8 =$ $2.5 \times 10^{-3}{:}1.8 \times 10^{-3}{:}2.5 \times 10^{-1}$ ${:}2.5 \times 10^{-3}{:}1.0$	296	Su, Calvert, and Shaw 1980[2]	(b)
$k_2/k_8 = (2.3 \pm 1) \times 10^{-4}$	298	Suto, Manzanares, and Lee, 1984[3]	(c)
$k_7/k_8 = (1.4 \pm 0.4) \times 10^{-2}$	298	Manzanares, Suto, and Lee, 1987[4]	(d)
Reviews and Evaluations			
$k_2 = 2 \times 10^{-19}$ to 1×10^{-15}	298	Herron, Martinez, and Huie, 1982[5]	(e)
$k_4 = 2 \times 10^{-16}$ to 8×10^{-13}	298		(f)
$k_7 = 1 \times 10^{-17}$ to 7×10^{-14}	298		(g)
$k_8 = 3 \times 10^{-15}$ to 1.7×10^{-11}	298		(h)
$k_2{:}k_3{:}k_4{:}k_6{:}k_7{:}k_8 = 298$ $5 \times 10^{-5}{:}2 \times 10^{-3}{:}0\ 25{:}10^2{:}10{:}1$	Atkinson and Lloyd, 1984[6]		(i)
$k_2 \sim 4 \times 10^{-18}$	298		
$k_4 \sim 2 \times 10^{-14}$	298		(j)
$k_6 = 7 \times 10^{-12}$	298		(k)
$k_7 \sim 7 \times 10^{-13}$	298		(j)
$k_8 \sim 7 \times 10^{-14}$	298		(j)
$k_2 = 4 \times 10^{-16}$	298	Kerr and Calvert, 1984[7]	(l)
$k_3 = 1.3 \times 10^{-14}$	298		(l)
$k_4 = 2 \times 10^{-12}$	298		(l)
$k_6 = 7 \times 10^{-12}$	298		(l)
$k_7 = 1.0 \times 10^{-13}$	298		(l)
$k_8 = 7 \times 10^{-12}$	298		(l)

Comments

(a) Derived from a reanalysis of the data of Cox and Penkett[8] 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_3CHOO.

(b) FTIR study of the C_2H_4–O_3 reaction in the presence of O_2–N_2 mixtures at a total pressure of 700 Torr and with added (i) CO, (ii) HCHO, or (iii) 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 $[O_3]$, $[SO_2]$, 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) Based on ratio $k_2/k_8 \simeq 6 \times 10^{-5}$, as derived by Calvert *et al.*[1] from data of Cox and Penkett,[8] and taking $3 \times 10^{-15} < k_8 < 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [see comment (i)].

(f) 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.*[9] and on thermochemical kinetic estimates of Nangia and Benson.[10] Details were not provided. It has been assumed that the reactivities of the CH_2OO and CH_3CHOO biradicals are identical.

(g) Derived from the ratio $k_4/k_7 \simeq 14$, which has been estimated[5] from data of Martinez *et al.*[20] from a study of the reduction in secondary ozonide formation in the O_3–O_2-*trans*-2-C_4H_8 reaction in the presence of NO_2. k_7 calculated by taking $2 \times 10^{-16} < k_4 < 8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} [see comment (f)]. It has been assumed that the reactivities of the CH_2OO and CH_3CHOO biradicals are identical.

(h) 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.*[9] and on thermochemical kinetic estimates of Nangia and Benson.[10] Details were not provided. It has been assumed that the reactivities of the CH_2OO and CH_3CHOO biradicals are identical.

(i) The relative rate coefficients are proposed on the basis that the data on CH_2OO (Su *et al.*[2]) and on CH_3CHOO (Cox and Penkett[8]) can be amalgamated, i.e., CH_2OO and CH_3CHOO have the same reactivities. From the studies of Akimoto *et al.*[11,12] on the O_3–C_2H_4 and C_3H_6 system, it is estimated that k_6:k_7:k_8 = $10^2$10:1.

(j) Calculated from above relative rate coefficients and assuming that $k_6 = 7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} [see comment (*k*)].

(k) This rate coefficient is assumed to have a similar value to that of the reaction of alkylperoxy radicals with NO, i.e., $RO_2 + NO \rightarrow RO + NO_2$, hence $k_6 = 7\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(l) 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[6] (ii) from the relative rate data of Calvert *et al.*,[1] Su *et al.*,[2] and of Suto *et al.*[3]

Preferred Values

No recommendation.

Comments on Preferred Values

Vibrationally excited Criegie intermediates or biradicals, RCHOO*, are produced from the reactions of O_3 with alkenes.[13] These species decompose unimolecularly to give molecular or radical products or undergo collisional deactivation to yield thermally equilibrated biradicals, RCHOO. 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 RCHOO with aldehydes[14,2,15,16,9,17] with SO_2[2,8,9,1,19] and with H_2O[8,1,11,18] 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 the consumption of SO_2, in systems involving RCHOO 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 about a factor of 4. Notwithstanding this discrepancy, these relative rate measurements are the only experimental basis on which to assess the rates of these reactions. It is apparent from these measurements that the reactions of the biradicals, CH_3CHOO, 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 forming acidic products.

Previous reviewers[6,7] have made the reasonable assumption that the reaction of RCHOO with NO could also be significant, based on estimates of the energetics of the proposed reaction pathway $RCHOO + NO \rightarrow RCHO + NO_2$. 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[6] have estimated the relative rate coefficients for RCHOO reacting with NO and SO_2 corresponding to $k_6/k_7 = 10^2$, whereas Kerr and Calvert[7] propose $k_6/k_7 = 1$. Experimental data on this ratio of rate coefficients are badly needed.

In the absence of direct kinetic measurements of the absolute rate coefficients of any of the RCHOO bimolecular reactions, both Atkinson and Lloyd[6] and Kerr and Calvert[7] have suggested that k_6 should be equated to the rate coefficient for the structurally analogous reactions, $RO_2 + NO \rightarrow RO + NO_2$, i.e., $k_6 = 7\times10^{-12}$ 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 RCHOO systems involving O_3-alkene reactions owing to the complex chemistry involved. In this regard the recent studies of Hatakeyama *et al.*[18] involving the generation of CH_2OO from the reaction of CH_2 ($^3B_1$) with O_2 are of considerable interest.

In deriving the relative rate coefficients listed above, it has been necessary to compare data obtained from different O_3-alkene systems and to assume that all the RCHOO biradicals have equal reactivity, e.g., CH_2OO and CH_3CHOO. Again, while this seems to be a reasonable assumption, it requires experimental verification.

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

$\Delta H^\circ(1) = -26\ \text{kJ mol}^{-1}$
$\Delta H^\circ(2) = -455\ \text{kJ mol}^{-1}$

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

$k/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.35×10^{-11}	298	Whyte and Phillips, 1983[1]	(a)
$(2.5\pm0.2)\times10^{-11}$	295	Lichtin and Lin, 1985[2]	(b)
$(1.86\pm0.20)\times10^{-11}$	295	de Juan, Smith, and Veyret, 1987[3]	(c)
$(1.82\pm0.12)\times10^{-11}$	300	Anastasi and Hancock, 1988[4]	(d)
$(1.25\pm0.16)\times10^{-11}\exp[(205\pm48)/T]$	294–761	Sims and Smith, 1988[5]	(c)
$(2.45\pm0.10)\times10^{-11}$	294		
Reviews and Evaluations			
$7.0\times10^{-11}\exp(-450/T)$	290–400	CODATA, 1984[6]	(e)

Comments

(a) Laser-pulsed photolysis of $(CN)_2$ in a fast-flow system with Ar carrier gas and LIF determination of [CN]. k determined under pseudo-first-order conditions with $[O_2] > [CN]$ at total pressures of ~2 Torr.

(b) Laser-pulsed photolysis of ICN in a flow system with Ar carrier gas and LIF determination of [CN]. k determined under pseudo-first-order conditions with $[O_2] > [CN]$ at total pressures of 16 and 50 Torr.

(c) Laser-pulsed photolysis of ICN in a flow system with Ar carrier gas and LIF determination of [CN]. k determined under pseudo-first-order conditions with $[O_2] > [CN]$ at total pressures of 10–30 Torr.

(d) Flash photolysis of $(CN)_2$ in Ar in a flow system with LIF determination of [CN]. k determined under pseudo-first-order conditions with $[O_2] > [CN]$ at total pressures of ~20 Torr.

(e) Based on data of Li *et al.*[7] and the evaluation of Baulch *et al.*[8]

Preferred Values

$k = 2.1\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ at 298 K.

$k = 1.1\times10^{-11}\exp(205/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ over range 290–760 K.

$k_1/k = 0.94$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 200$ K.
$\Delta (k_1/k) = \pm 0.06$.

Comments on Preferred Values

There is reasonably good agreement amongst the recent determinations of the room-temperature rate coefficient of this reaction, which have involved the technique of laser-induced fluorescence to monitor the kinetic behavior of the CN radical. The preferred rate coefficient at 298 K is a mean of the results of Li *et al.*,[7] Lichtin and Lin,[2] de Juan *et al.*,[3] Anastasi and Hancock,[4] and Sims and Smith.[5]

The recommended temperature coefficient is that reported by Sims and Smith, with adjustment of the A-factor to agree with the recommended k_{298}. While this negative temperature dependence of the rate coefficient is consistent with the shock-tube study of Louge and Hanson,[9] ($k = 8.0\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ at 2400 K) confirmation of the temperature coefficient is required.

The branching ratio reported by Schmatjko and Wolfrum[10] is again accepted, but this also requires to be substantiated.

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$O_3 + C_2H_2 \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.8 \pm 2.8) \times 10^{-20}$	303	Cadle and Schadt, 1953[1]	(a)
$(5.3^{+7.9}_{-3.2}) \times 10^{-12} \exp[-(5435 \pm 201)/T]$	243–283	DeMore, 1969[2]	(b)
6.4×10^{-20}	298*		
$(3.0 \pm 0.5) \times 10^{-20}$	294	DeMore, 1971[3]	(c)
$(8.6 \pm 0.9) \times 10^{-20}$	298	Stedman and Niki, 1973[4]	(d)
$(3.8 \pm 0.6) \times 10^{-20}$	297	Pate, Atkinson, and Pitts, 1976[5]	(d)
$(7.8 \pm 1.2) \times 10^{-21}$	294	Atkinson and Aschmann, 1984[6]	(d)

Comments

(a) Static system with infrared absorption detection of O_3 and C_2H_2. An approximate temperature dependence of 20 kJ mol^{-1} was reported.

(b) Static system with ultraviolet absorption detection of O_3 at 253.7 nm.

(c) Static system with ultraviolet (253.7 nm) and/or infrared (1053 cm^{-1}) absorption detection of O_3.

(d) Static system with chemiluminescence detection of O_3.

Preferred Values

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

Reliability

$\Delta \log k = \pm 1.0$ at 298 K.

Comments on Preferred Values

The literature data show a large degree of scatter at room temperature. While the most recent and lowest rate coefficient of Atkinson and Aschmann[6] may be the most correct (any impurities would lead to higher rate constants), the preferred value and its associated large uncertainty cover the available 298 K rate coefficients. No recommendation is made regarding the temperature dependence.

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$O_3 + C_2H_4 \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.6 \pm 1.4) \times 10^{-18}$	303–323	Cadle and Schadt, 1952[1]	(a)
1.35×10^{-18}	~298	Hanst *et al.*, 1958[2]	(b)
$2.8 \times 10^{-15} \exp[-(2114 \pm 201)/T]$	303–373	Bufalini and Altshuller, 1965[3]	(c)
$(2.66 \pm 0.33) \times 10^{-18}$	303		
3.3×10^{-18}	298	Bufalini and Altshuller, 1965[3]	(d)
$(3.3^{+5.0}_{-2.0}) \times 10^{-15} \exp[-(2365 \pm 101)/T]$	178–233	DeMore, 1969[4]	(e)
1.18×10^{-18}	298*		
$(1.55 \pm 0.15) \times 10^{-18}$	299	Stedman, Wu, and Niki, 1973[5]	(f)
$1.2 \times 10^{-14} \exp[-(2491 \pm 101)/T]$	~284–347	Becker, Schurath, and Seitz, 1974[6]	(g)
2.8×10^{-18}	298		
$(9.00 \pm 5.30) \times 10^{-15}$ $\exp[-(2557 \pm 167)/T]$	235–362	Herron and Huie, 1974[7]	(h)
1.69×10^{-16}	298		
$(1.9 \pm 0.1) \times 10^{-18}$	299	Japar, Wu, and Niki, 1974[8]	(f)
$(1.9 \pm 0.1) \times 10^{-18}$	299	Japar, Wu, and Niki, 1976[9]	(f)
$(1.69 \pm 0.13) \times 10^{-18}$	303	Toby, Toby, and O'Neal, 1976[10]	(e)
$(1.8 \pm 0.1) \times 10^{-18}$	298	Su, Calvert and Shaw, 1980[11]	(i)
$3.2 \times 10^{-14} \exp(-2920/T)$	260–294	Adeniji, Kerr, and Williams, 1981[12]	(f)
1.6×10^{-18}	294		
1.8×10^{-18}	~298	Niki *et al.*, 1981[13]	(i)
$(2.6^{+2.2}_{-1.2}) \times 10^{-14} \exp[-(2828 \pm 181)/T]$	283–304	Kan *et al.*, 1981[14]	(i,j)
1.97×10^{-18}	298		
$(1.43 \pm 0.19) \times 10^{-18}$	296	Atkinson *et al.*, 1982[15]	(f)
$(7.72 \pm 0.89) \times 10^{-15} \exp[-(2557 \pm 30)/T]$	232–298	Bahta, Simonaitis, and Heicklen, 1984[16]	(e)
$(1.45 \pm 0.10) \times 10^{-18}$	298		
Reviews and Evaluations			
$1.20 \times 10^{-14} \exp(-2633/T)$	178–362	Atkinson and Carter, 1984[17]	(k)

Comments

(a) Static system, with infrared absorption detection of C_2H_4 and O3.

(b) Both static and stirred flow reaction systems were used, with infrared absorption spectroscopic detection.

(c) Stirred flow reactor used with wet chemical analysis of O_3.

(d) Static system with wet chemical analysis of O_3.

(e) Static system, with ultraviolet absorption detection of O_3 at 253.7 nm.

(f) Static system, with chemiluminescence detection of O_3.

(g) Static system, with ultraviolet absorption detection of O_3 at 253.7 nm. Low total pressures used, and it was noted that insufficient O_2 was present to minimize the occurrence of secondary reactions. Hence these data are upper limits to the elementary rate coefficients.

(h) Stopped flow system, with mass spectrometric detection of O_3. Carried out at total pressure of ~4 Torr, but with sufficient O_2 present to minimize the occurrence of secondary reactions removing O_3.

(i) Static system, with analysis of O_3 and C_2H_4 by Fourier transform infrared (FT–IR) absorption spectroscopy.

(j) Arrhenius expression derived from the data of Su *et al.*[11] and Kan *et al.*,[14] both of these studies being conducted by the same research group using the same experimental techniques.

(k) Derived from the rate coefficient data of DeMore,[4] Stedman *et al.*,[5] Herron and Huie,[7] Japar *et al.*,[8,9] Toby *et al.*,[10] Su *et al.*,[11] Adeniji *et al.*,[12] Kan *et al.*,[14] and Atkinson *et al.*[15] The earlier data of Cadle and Schadt[1] and Bufalini and Altshuller[3] were not used because of questions regarding the validity of the experimental methods used, those of Hanst *et al.*[2] and Niki *et al.*[13] could not be used since the temperature was not specified, and the rate coefficients of Becker *et al.*[6] are recognized to be erroneously high due to the presence of insufficient O_2 to avoid or minimize secondary reactions removing O_3.

Preferred Values

$k = 1.7\times10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.2\times10^{-14}\exp(-2630/T)$ cm^3 molecule^{-1} s^{-1} over the range 180–360 K.

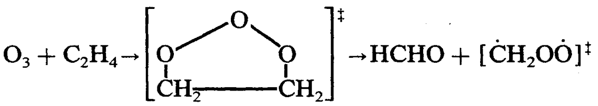
Reliability

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

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

Comments on Preferred Values

Derived from the data set[4,5,8-12,14,15] utilized by Atkinson and Carter,[17] together with the more recent rate coefficients measured by Bahta *et al.*[16] (averaging the individual data given at each temperature studied to provide a single rate constant for each of the temperatures 232, 251, 272, and 298 K). As discussed by Atkinson and Lloyd[18] and Atkinson and Carter,[17] the initial reaction forms the energy rich trioxane which rapidly decomposes



to yield HCHO and the energy-rich biradical $[\dot{C}H_2O\dot{O}]^\ddagger$.

This energy rich biradical can either decompose or be stabilized

$$[\dot{C}H_2O\dot{O}]^\ddagger \rightarrow CO_2 + H_2 \quad (a)$$
$$[\dot{C}H_2O\dot{O}]^\ddagger \rightarrow CO + H_2O \quad (b)$$
$$[\dot{C}H_2O\dot{O}]^\ddagger \rightarrow H + HCO_2 \rightarrow 2HO_2 + CO_2 \quad (c)$$
$$[\dot{C}H_2O\dot{O}]^\ddagger \xrightarrow{M} \dot{C}H_2O\dot{O}. \quad (d)$$

At room-temperature and atmospheric pressure, the fraction of stabilization is 0.37,[11,13,14,19] and the fractions of the overall reactions proceeding via pathways (a) through (c) are then approximately 0.13, 0.44, and 0.06, respectively.[17,18] The relative importance of these decomposition/stabilization reactions of the $[\dot{C}H_2O\dot{O}]^\ddagger$ radical are, however, pressure dependent, with no quantitative data being available other than at ~760 Torr total pressure of air.

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$O_3 + C_3H_6 \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
6.2×10^{-18}	~298	Cadle and Schadt, 1952[1]	(a)
8.1×10^{-18}	~298	Hanst *et al.*, 1958[2]	(b)
1.26×10^{-17}	296	Cox and Penkett, 1972[3]	(c)
$(1.25 \pm 0.10) \times 10^{-17}$	299	Stedman, Wu, and Niki, 1973[4]	(d)
$1.10 \times 10^{-14} \exp[-(1968 \pm 101)/T]$	286–358	Becker, Schurath, and Seitz, 1974[5]	(e)
1.45×10^{-17}	298		
$(6.14 \pm 2.36) \times 10^{-15} \exp[-(1897 \pm 109)/T]$	250–362	Herron and Huie, 1974[6]	(f)
1.06×10^{-17}	298		
$(1.30 \pm 0.01) \times 10^{-17}$	299	Japar, Wu, and Niki, 1974[7]	(d)
$(1.32 \pm 0.03) \times 10^{-17}$	299	Japar, Wu, and Niki, 1976[8]	(d)
$1.3 \times 10^{-14} \exp -(2013/T)$	260–294	Adeniji, Kerr, and Williams, 1981[9]	(d)
1.26×10^{-17}	294		
$(1.04 \pm 0.14) \times 10^{-17}$	296	[illegible]inson *et al.*, 1982[10]	(d)
Reviews and Evaluations			
$1.32 \times 10^{-14} \exp(-2105/T)$	250–362	Atki[illegible]nd Carter, 1984[11]	(g)

Comments

(a) Static system, with wet chemical analysis for oxidant.

(b) Both static and stirred flow reaction systems were used, with infrared absorption spectroscopic detection.

(c) Static system with detection of O_3 by both chemiluminescence and wet chemical analysis.

(d) Static system, with chemiluminescence detection of O_3.

(e) Static system, with ultraviolet absorption detection of O_3 at 253.7 nm. Low total pressures used, and it was observed that the presence of O_2 was necessary to minimize the occurrence of secondary reactions. It is possible that these data are still upper limits to the elementary rate coefficients.

(f) Stopped flow system, with mass spectrometric detection of O_3. Carried out at total pressure of ~4 Torr, but with sufficient O_2 present to minimize the occurrence of secondary reactions removing O_3.

(g) Derived from the rate coefficients of Cox and Penkett,[3] Stedman *et al.*,[4] Herron and Huie,[6] Japar *et al.*,[7,8] Adeniji *et al.*,[9] and Atkinson *et al.*[10] The earlier data of Cadle and Schadt[1] were not used because of questions concerning the validity of the wet chemical analysis used, and in any case the temperature was not specified. This was also the case for the study of Hanst *et al.*[2] The data of Becker *et al.*[5] were not utilized in the evaluation since they were ~40% higher than the other data used,[3,4,6–10] possibly due to the presence of insufficient O_2 to avoid secondary reactions.

Preferred Values

$k = 1.1 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3 \times 10^{-14} \exp(-2105/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–360 K.

Reliability

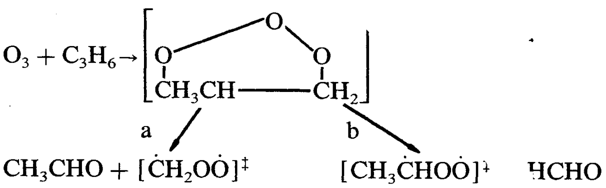
$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta (E/R) = \pm 400$ K.

Comments on Pre[illegible]d Values

Accepts the eva[illegible]ion of Atkinson and Carter,[11] which was derived from a leas[illegible]uares analysis of the data of Refs. 3, 4, and 6–10.

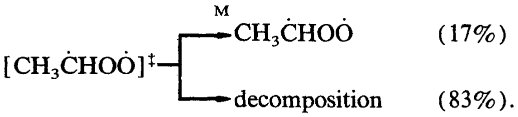
The reaction proceeds [illegible] formation of a trioxane, which rapidly decomposes:



The rate coefficient ratio k_a/k_b has not been experimentally determined, and is assumed to be approximately unity. It is generally assumed[11,12] 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 ~760 Torr total pressure of air[11–13]

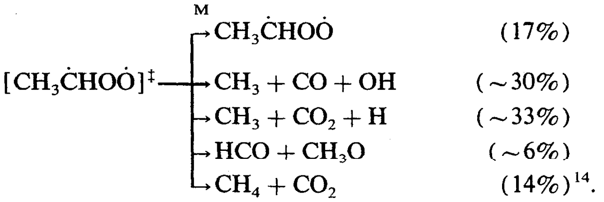
$[\dot{C}H_2O\dot{O}]^{\ddagger}$	$\rightarrow CO_2 + H_2$	~13%
	$\rightarrow CO + H_2O$	~44%
	$\rightarrow 2HO_2 + CO$	~6%
$[\dot{C}H_2O\dot{O}]^{\ddagger} + M$	$\rightarrow \dot{C}H_2O\dot{O} + M$	37%.

Less data are available concerning the stabilization and decomposition reactions of the $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ biradical. Based upon the SO_2 to H_2SO_4 conversion yield in an O_3 + propene reaction system, Hatakeyama *et al.*[13] 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. 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 $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ biradicals which are stabilized at ~298 K and 760 Torr total air pressure is 0.14. This value agrees well with the measured yields of stabilized $CH_3\dot{C}HO\dot{O}$ from *trans*-2-butene (0.185[13]) and *cis*-2-butene (0.18[14]). A yield of stabilized $CH_3\dot{C}HO\dot{O}$ from $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ of 0.17 at 298 K and 760 Torr total pressure of air is recommended:



$$[\mathrm{CH_3\dot{C}HO\dot{O}}]^{\ddagger} \begin{cases} \xrightarrow{M} \mathrm{CH_3\dot{C}HO\dot{O}} & (17\%) \\ \rightarrow \text{decomposition} & (83\%). \end{cases}$$

The decomposition pathways are less well understood,[11,12] but are expected to involve formation of $CH_3 + CO + OH$, $CH_3 + CO_2 + H$, $HCO + CH_3O$, and $CH_4 + CO_2$, with approximate fractional overall yields of ~0.3, ~0.3–0.35, ~0.06, and 0.14,[11,12,14] i.e.,



$$[\mathrm{CH_3\dot{C}HO\dot{O}}]^{\ddagger} \begin{cases} \xrightarrow{M} \mathrm{CH_3\dot{C}HO\dot{O}} & (17\%) \\ \rightarrow \mathrm{CH_3 + CO + OH} & (\sim 30\%) \\ \rightarrow \mathrm{CH_3 + CO_2 + H} & (\sim 33\%) \\ \rightarrow \mathrm{HCO + CH_3O} & (\sim 6\%) \\ \rightarrow \mathrm{CH_4 + CO_2} & (14\%)^{14}. \end{cases}$$

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$HCHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$HCHO + h\nu \rightarrow H + HCO$	(1)	358.4	334
$\rightarrow H_2 + CO$	(2)	−9.1	···

Absorption cross-section data

Wavelength range/nm	Reference	Comments
253.0–353.1	Moortgat, Seiler, and Warneck, 1983[1]	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength/nm	Reference	Comments
ϕ, ϕ_2/ϕ	253–353	Moortgat, Seiler, and Warneck, 1983[1]	(b)
$\phi_1 = 0.70 \pm 0.06$	313	Carmely and Horowitz[2]	(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) Quantum yields of CO_2 and H_2 were measured as a function of wavelengths of 253–354 nm for HCHO at low concentration in air. Previous results on the pressure and temperature dependences of ϕ_1 and ϕ_2 were confirmed.[3]

(c) Study of the photo-oxidation of formaldehyde in $HCHO–O_2$, oxygen lean mixtures over the temperature range 298–378 K, which extend a previous study[4] at 373 K. ϕ_1 obtained from measurements in which isobutene was used as a scavenger for H atoms.

Preferred Values

Absorption cross sections and quantum yields for HCHO photolysis[a]

	$10^{20}\sigma$/cm^2			
Wavelength/nm	200 K	298 K	ϕ_1	ϕ_2
240	0.02	0.08	0.27	0.49
250	0.22	0.31	0.29	0.49
260	0.51	0.54	0.30	0.49
270	0.96	0.95	0.38	0.43
280	1.77	1.80	0.57	0.32
290	3.05	2.93	0.73	0.24
300	4.00	4.06	0.78	0.21
310	4.58	4.60	0.78	0.22
320	4.18	4.15	0.62	0.38
330	3.20	3.21	0.27	0.66
340	2.18	2.22	0.00	0.56
350	1.25	1.25	0.00	0.21
360	0.23	0.18	0.00	0.03

[a] Values averaged for 10 nm intervals of wavelength centered on indicated wavelength.

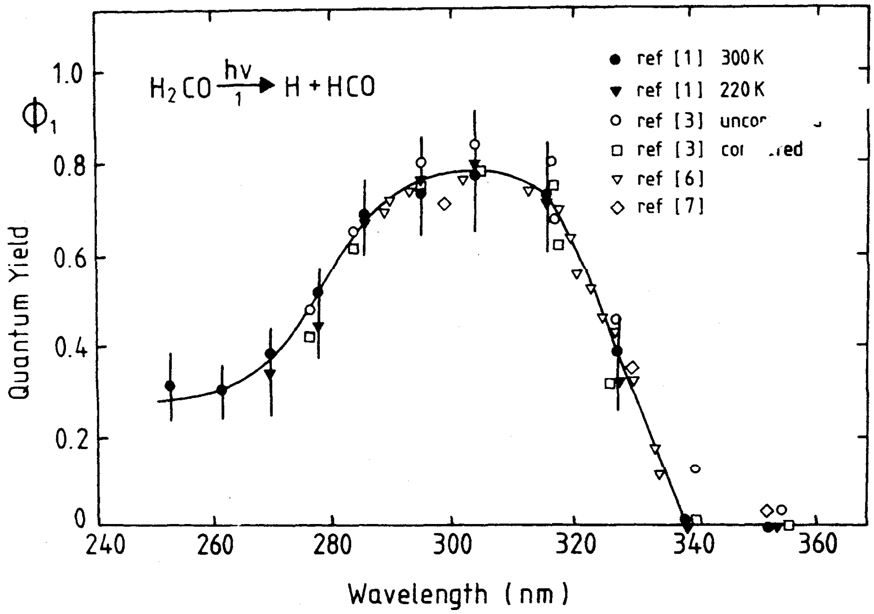

FIG. 2. Wavelength dependence of HCHO photolysis quantum yield (ϕ_1) for radical formation.

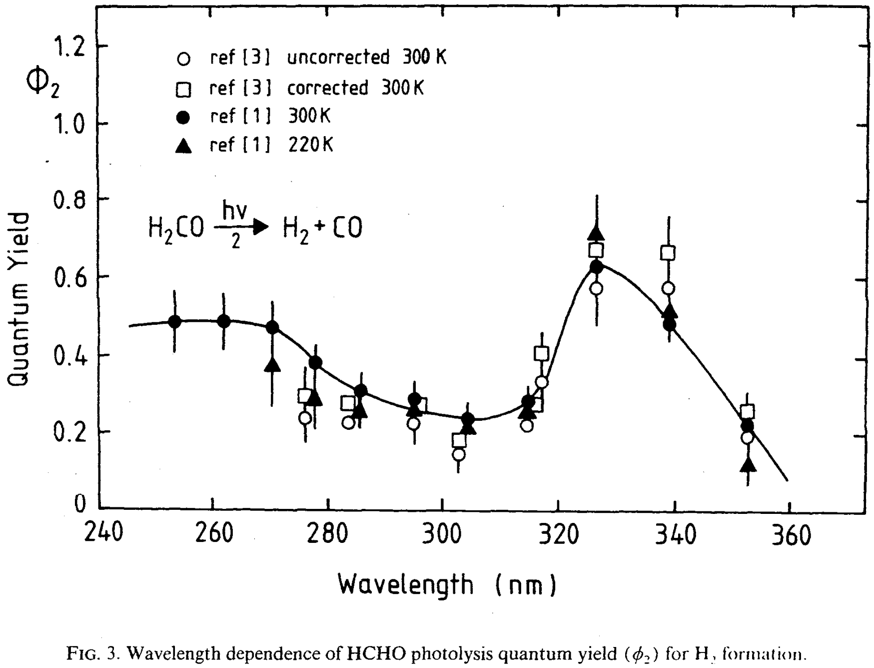

FIG. 3. Wavelength dependence of HCHO photolysis quantum yield (ϕ_2) for H_2 formation.

Absorption cross sections for HCHO photolysis, $T = 285$ K[a]

Wavelength/nm	$10^{20}\sigma/\mathrm{cm}^2$	Wavelength/nm	$10^{20}\sigma/\mathrm{cm}^2$
240	0.064	301	1.715
241	0.056	302	1.064
242	0.105	303	3.201
243	0.115	304	6.902
244	0.082	305	4.914
245	0.103	306	4.632
246	0.098	307	2.100
247	0.135	308	1.494
248	0.191	309	3.407
249	0.282	310	1.950
250	0.205	311	0.521
251	0.170	312	1.120
252	0.288	313	1.116
253	0.255	314	4.747
254	0.255	315	5.247
255	0.360	316	2.899
256	0.509	317	5.373
257	0.339	318	2.975
258	0.226	319	0.918
259	0.504	320	1.262
260	0.505	321	1.529
261	0.549	322	0.669
262	0.520	323	0.345
263	0.933	324	0.816
264	0.823	325	1.850
265	0.430	326	5.950
266	0.495	327	3.485
267	1.239	328	1.087
268	1.110	329	3.353
269	0.878	330	3.321
270	0.936	331	1.073
271	1.789	332	0.289
272	1.227	333	0.215
273	0.645	334	0.171
274	0.656	335	0.143
275	2.232	336	0.194
276	2.416	337	0.417
277	1.402	338	2.360
278	1.050	339	4.712
279	2.548	340	2.481
280	2.083	341	0.759
281	1.475	342	0.681
282	0.881	343	1.953
283	1.066	344	1.137
284	4.492	345	0.323
285	3.592	346	0.113
286	1.962	347	0.066
287	1.295	348	0.122
288	3.356	349	0.032
289	2.838	350	0.038
290	1.304	351	0.104
291	1.746	352	0.713
292	0.832	353	2.212
293	3.727	354	1.536
294	6.535	355	0.676
295	3.950	356	0.135
296	2.333	357	0.036
297	1.513	358	0.0057
298	4.037	359	0.058
299	2.871	360	0.082
300	0.871		

[a] Averaged over 0.5 nm wavelength intervals centered at the cited wavelength [G. K. Moortgat and W. Schneider (unpublished data)].

Comments on Preferred Values

The preferred values of the absorption cross sections and the primary quantum yields are taken from the results of Moortgat *et al.*,[1] averaged over two wavelength intervals (0.5 and 10 nm), which are basically the same data as listed in our previous evaluation.[5] The slight changes in the values of the cross sections, compared with the previous recommendation, are due to the extrapolation procedure mentioned in comment (a), which was not previously carried out. Likewise, the slightly amended quantum yields, ϕ_1 and ϕ_2, are believed[1] to have arisen from small systematic errors in the calibration procedures for H_2 and CO thought to be involved with the original experiments.

The updated plots of the wavelength dependence of the HCHO quantum yields are shown in Figs. 2 and 3. It should, however, be mentioned that there is a problem in understanding the measured quantum yields and branching ratios $Y_2 = \phi_2(\phi_1 + \phi_2)$. 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 $H_2CO^* \rightarrow H + HCO$ or $H_2CO^* \rightarrow H_2 + CO$, the measured values of Y_2 for $\lambda \lesssim 300$ nm would be difficult to interpret. Simulations[6] of the rates of the competing processes of H_2CO^* and measurements of the product yields in molecular beams[7] would indicate that the radical channel $H_2CO^* \rightarrow H + HCO$ dominates for $\lambda \lesssim 300$ nm, with $Y_2 \leqslant 0.1$ at 284 nm.[7] An analysis of the details of the photophysical processes[8] has failed to resolve this discrepancy with the macroscopic photochemical observations. The branching ratios for $\lambda \lesssim 300$ nm should therefore be treated with caution.

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$CH_3CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298} /kJ mol^{-1}	$\lambda_{threshold}$ /nm
$CH_3CHO + h\nu$	$\rightarrow CH_4 + CO$ (1)	-25.4	...
	$\rightarrow CH_3 + HCO$ (2)	349.0	342.8
	$\rightarrow CH_3CO + H$ (3)	359.9	332.4

Quantum yield data ($\Phi = \Phi_1 + \Phi_2 + \Phi_3$)

Measurement			Wavelength/nm	Reference	Comments
$\Phi_1 = 0.47$	$\Phi_2 = 0.31$		260	Atkinson and Lloyd, 1984[1]	(a)
$\Phi_1 = 0.33$	$\Phi_2 = 0.38$		270		
$\Phi_1 = 0.06$	$\Phi_2 = 0.59$		280		
$\Phi_1 = 0.01$	$\Phi_2 = 0.55$	$\Phi_3 = 0.026$	290		
$\Phi_1 = 0.00$	$\Phi_2 = 0.415$	$\Phi_3 = 0.009$	300		
$\Phi_1 = 0.00$	$\Phi_2 = 0.235$		310		
		$\Phi_3 = 0.00$	313		
$\Phi_1 = 0.00$	$\Phi_2 = 0.08$	$\Phi_3 = 0.00$	320		
$\Phi_1 = 0.00$	$\Phi_2 = 0.00$		330		
		$\Phi_3 = 0.00$	331–2		

Comments

(a) Evaluation of data of Horowitz and Calvert[2] and of Meyrahn, Moortgat, and Warneck.[3]

Preferred Values

Absorption cross sections and quantum yields for CH_3CHO photolysis (Φ_1 and Φ_2 for 1 atm air)

Wavelength/nm	$10^{20}\sigma$/cm^2	Φ_1	Φ_2
200	0.77		
210	0.31		
220	$\leqslant 0.1$		
240	0.42		
250	1.0		
260	2.0	0.46	0.31
270	3.4	0.31	0.39
280	4.5	0.05	0.58
290	4.9	0.01	0.53
295	4.5	0.00	0.48
300	4.3		0.43
305	3.4		0.37
315	2.1	0.17	
320	1.8	0.10	
325	1.1	0.04	
330	0.69	0.00	
335	0.38		
340	0.15		
345	0.08		

Comments on Preferred Values

The evaluated data on Φ_1 and Φ_2 derived by Atkinson and Lloyd[1] from the experimental data of Horowitz and Calvert[2] and of Meyrahn, Moortgat, and Warneck[3] are in essential agreement with our previous recommendations,[4] which remain unaltered.

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[4] CODATA Supplement II, 1984 (See References in Introduction).

$C_2H_5CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reactions		ΔH°_{298} /kJ mol^{-1}	$\lambda_{\text{threshold}}$ /nm
$C_2H_5CHO \rightarrow C_2H_5 + HCO$	(1)	344.4	347.3
$\rightarrow C_2H_6 + CO$	(2)	− 4.2	...
$\rightarrow C_2H_4 + HCHO$	(3)	133.7	894.7
$\rightarrow CH_3 + CH_2CHO$	(4)	348.4	343.4

Absorption cross section data

Wavelength range/nm	Reference	Comments
200–300	Calvert and Pitts, 1966[1]	(a)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 \simeq 0.12$, $\phi_2 \simeq 0.51$, $\phi_3 \simeq 0.06$, $\phi_4 \simeq 0.31$	187	Calvert and Pitts, 1966[1]	(b)
$\phi_4 \simeq 0.08$	238		
$\phi_1 \geqslant 0.28$, $\phi_2 \geqslant 0.37$, $\phi_3 \simeq 0.013$, $\phi_4 \simeq 0.039$	253.7		
$\phi_1 \geqslant 0.28$, $\phi_2 \geqslant 0.34$, $\phi_3 \simeq 0.013$, $\phi_4 \simeq 0.012$	265.4		
$\phi_1 \geqslant 0.53$, $\phi_2 \geqslant 0.13$, $\phi_3 \simeq 0.01$, $\phi_4 \simeq 0.007$	280.4		
$\phi_1 \geqslant 0.48$, $\phi_2 \simeq 0.022$, $\phi_3 \simeq 0.003$, $\phi_4 \simeq 0.00$	313		
$\phi_1 = 0.30 \pm 0.05$	313	Shepson and Heicklen, 1982[2]	(c)
$\phi_1 = 0.13$	254	Shepson and Heicklen, 1982[3]	(d)
$\phi_1 = 0.28$	280		
$\phi_1 = 0.22$	302		
$\phi_1 = 0.26$	313		
$\phi_1 = 0.067$	326		
$\phi_1 = 0.18$	334		
$\phi_1 = 0.89$	294	Heicklen *et al.*, 1986[4]	(d)
$\phi_1 = 0.85$	302		
$\phi_1 = 0.50$	313		
$\phi_1 = 0.26$	325		
$\phi_1 = 0.15$	334		

Comments

(a) Spectra recorded in a 10 cm cell at 298 K and at several different pressures of C_2H_5CHO. Data presented as a plot of ϵ/dm^3 mol^{-1} cm^{-1} versus wavelength.

(b) Summary of earlier data of Blacet and Pitts,[5] Blacet and Crane,[6] and Borkowski and Ausloos.[7]

(c) Steady-state photolysis of C_2H_5CHO at 313 nm and 295 K in presence of O_2, O_2–He, O_2–N_2, O_2–NO, and O_2-*cis*-2-C_4H_8 mixtures. Quantum yields for CO and other products measured as a function of $[O_2]$, $[C_2H_5CHO]$, etc. ϕ_{CO} measurements indicate that $C_2H_5CHO^*$ from absorption is pressure quenched and quoted value of ϕ_1 is for 1 atm of air.

(d) An extension of the experiments of Shepson and Heicklen[2] at a range of wavelengths and at 296 K. Quoted values of ϕ_1 are for 1 atm of air.

(e) Flash photolysis of C_2H_5CHO in the presence of air and steady-state photolysis of C_2H_5CHO in presence of O_2 at 263 or 298 K. Quantum yields of CO and C_2H_6 were measured as a function of λ and of pressure of added O_2. From the proposed mechanism it was deduced that $\phi_1 = \Phi_{CO} - \Phi_{C_2H_6}$; values of ϕ quoted are for 1 atm of air.

Preferred Values

Wavelength/nm	$10^{20}\sigma$/cm^2	ϕ_1
230	0.00	
240	0.46	
250	1.1	
260	2.4	
270	4.1	
280	5.2	
290	5.7	
294		0.89
300	5.0	
302		0.85
310	3.7	
313		0.50
320	1.9	
325		0.26
330	0.80	
334		0.15
340	0.26	

Comments on Preferred Values

The preferred values of the absorption cross sections were taken from the plot of the extinction coefficient as a function of wavelength reported by Calvert and Pitts,[1] and are the actual values for the wavelengths indicated rather than averaged values.

The preferred values of the quantum yields for the photodissociation yielding C_2H_5 radicals are taken from the study of Heicklen *et al.*,[3] and refer to photolysis in air at a total pressure of 1 atm. No explanation has been put forward to account for the large differences in the reported values of ϕ_1 as a function of wavelength.[3,4]

References

[1] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).
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[6] F. E. Blacet and R. A. Crane, J. Am. Chem. Soc. **76**, 5337 (1954).
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$(CHO)_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reactions		ΔH°_{298}/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$(CHO)_2 + h\nu \rightarrow H_2 + 2CO$	(1)	-9.1	···
$\rightarrow 2HCO$	(2)	286.4	417.7
$\rightarrow CH_2O + CO$	(3)	-7.2	···

Absorption cross section data

Wavelength range/nm	Reference	Comments
230–462	Plum *et al.*, 1983[1]	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength/nm	Reference	Comments
$\phi_1/\phi_3 \simeq 0.19$	253.7	Calvert and Pitts, 1966[2]	(b)
$\phi_1 \simeq 0.15$, $\phi_2 \simeq 0.0$, $\phi_3 \simeq 0.85$	313		
$\phi_1/\phi_3 \simeq 0.03$, $\phi_2 \simeq 0.0$	366		
$\phi_1 \simeq 0.01$, $\phi_3 \simeq 0.6$	435.8		
$\phi = 0.029 \pm 0.018$	325–470	Plum *et al.*, 1983[1]	(c)
$\phi_2 = 0.4 \pm 0.2$	308	Langford and Moore, 1984[3]	(d)

Comments

(a) Measured with a Cary 17-D spectrophotometer at glyoxal pressures of ~3–13 Torr.

(b) Review of earlier data of Blacet and Moulton,[4] Calvert and Layne,[5] Herzberg and Ramsay,[6] and Parmenter.[7]

(c) Study of the rate of photolysis of glyoxal in air mixtures at atmospheric pressure in an environmental smog chamber. The quantum yield for the photodissociation of glyoxal was obtained by dividing the observed ratio of the rate of photolysis of glyoxal to the rate of photolysis of NO_2 (under similar experimental conditions), by the same ratio calculated on the assumption that $\phi_\lambda = 1$ for glyoxal.

(d) Laser photolysis of 4.0 Torr glyoxal in 1000 Torr N_2 at 295 K. HCO product determined by time-resolved laser resonance absorption. Quantum yield determined by comparing radical signals following CH_2O and $(HCO)_2$ photolyses.

Preferred Values

Absorption cross sections for glyoxal

Wavelength/nm	$10^{20}\sigma/\text{cm}^2$	Wavelength/nm	$10^{20}\sigma/\text{cm}^2$	Wavelength/nm	$10^{20}\sigma/\text{cm}^2$
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 listed above are taken from the results of Plum *et al.*[1] and are in good agreement with earlier published data summarized by Calvert and Pitts.[2]

The selection of preferred quantum yields for the photolysis of glyoxal as a function of wavelength under atmospheric conditions must await further investigations. The "effective" quantum yield, $\phi = 0.029$, reported by Plum *et al.*[1] is strictly valid only for the particular spectral distributions used in their study. This value of ϕ may be used to calculate the rates of photolyses of glyoxal under tropospheric conditions within the spectral region 325–470 nm. For the lower wavelength band in the troposphere it is recommended that the value $\phi = 0.4$, reported by Langford and Moore[3] at 308 nm, be used in such calculations.

References

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

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[5] J. G. Calvert and G. S. Layne, J. Am. Chem. Soc. **75**, 856 (1953).

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$CH_3COCHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reactions		ΔH°_{298}/kJ mol^{-1}	$\lambda_{threshold}$ /nm
$CH_3COCHO + h\nu \rightarrow CH_4 + 2CO$	(1)	-24.8	...
$\rightarrow CH_3CO + HCO$	(2)	284.0	421
$\rightarrow CH_3CHO + CO$	(3)	-5.6	...

Absorption cross section data

Wavelength range/nm	Reference	Comments
220–466	Plum *et al.*, 1983[1]	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 + \phi_3 = 0.77$ $\phi_2 = 0.18$	436	Kyle and Orchard, 1977[2]	(b)
$\phi = 0.107 \pm 0.030$	325–470	Plum *et al.*, 1983[1]	(c)

Comments

(a) Measured with a Cary 17-D spectrophotometer at methylglyoxal pressures of ~3–13 Torr.

(b) Based on the quantum yields of products, CO, CH_4, C_2H_6, CH_3CHO, CH_3COCH_3 and $(CH_3CO)_2$ from the photolysis of methylglyoxal at 353–412 K over the pressure range 12–50 Torr of methylglyoxal and with added N_2 (30–175 Torr).

(c) Study of the rate of photolysis of methylglyoxal in air mixtures at atmospheric pressure in an environmental smog chamber. The quantum yield for the photodissociation of methylglyoxal was obtained by dividing the observed ratio, of the rate of photolysis of methylglyoxal to the rate of photolysis of NO_2 (under similar experimental conditions) by the same ratio calculated on the assumption that $\phi_\lambda = 1$ for methylglyoxal.

Preferred Values

Absorption cross sections for methylglyoxal

Wavelength/nm	$10^{20}\sigma$/cm^2	Wavelength/nm	$10^{20}\sigma$/cm^2
220	0.42	335–350	0.00
225	0.42	354	0.04
230	0.84	358	0.13
235	1.51	360	0.21
240	1.85	362	0.21
245	1.68	364	0.29
250	1.85	366	0.34
255	1.85	368	0.42
260	1.93	370	0.55
265	2.10	372	0.59
270	2.52	374	0.76
275	2.85	376	0.80
280	3.02	378	0.88
285	2.85	380	1.01
290	2.95	382	1.10
295	2.35	384	1.35
300	2.26	386	1.52
305	1.85	388	1.73
310	1.26	390	2.06
315	1.09	392	2.11
320	0.67	394	2.32
325	0.34	396	2.49
330	0.17	398	2.61

Absorption cross sections for methylglyoxal

Wavelength/nm	$10^{20}\sigma$/cm^2	Wavelength/nm	$10^{20}\sigma$/cm^2
400	2.78	439	6.66
402	2.99	440	5.48
404	3.20	441	6.15
406	3.79	442	5.48
408	3.96	443	6.82
410	4.34	444	5.98
412	4.72	445	5.14
414	4.80	446	4.89
416	4.89	447	5.73
418	5.06	448	5.48
420	5.22	449	6.57
422	5.31	450	5.06
424	5.18	451	3.03
426	5.31	452	4.30
428	5.22	453	2.78
430	5.56	454	2.28
432	5.14	456	1.77
433	5.98	458	0.84
434	5.69	460	0.42
435	6.49	462	0.29
436	6.24	464	0.17
437	5.22	466	0.00
438	6.07		

Comments on Preferred Values

The preferred values listed above are taken from the results of Plum *et al.*,[1] which appear to be the sole published data.

The selection of preferred quantum yields for the photolysis of methylglyoxal as a function of wavelength under atmospheric conditions must await further investigations. The "effective" quantum yield, $\phi = 0.107$, reported by Plum *et al.*[1] is strictly valid only for the particular spectral distribution used in their study. This value of ϕ may be used to calculate the rates of photolyses of methylglyoxal under tropospheric conditions within the spectral region 325–470 nm.

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] E. Kyle and S. W. Orchard, J. Photochem. 7, 305 (1977).

$CH_3COCH_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	ΔH°_{298}/kJ mol^{-1}	$\lambda_{\text{threshold}}$ /nm
$CH_3COCH_3 + h\nu \rightarrow CH_3CO + CH_3$ (1)	338.5	353
$\rightarrow 2CH_3 + CO$ (2)	397.9	300

Absorption cross section

Wavelength range/nm	Reference	Comments
200–340	Calvert and Pitts, 1966[1]	(a)
250–350	Meyrahn *et al.*, 1986[2]	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength/nm	Reference	Comment
$\phi_2/\phi = 0.07$	313	Calvert and Pitts, 1966[1]	(c)(e)
$\phi = 1.00$	313		(c)(d)
$\phi_2/\phi = 0.22$	253.7		(c)(e)
$\phi = 1.00$	253.7		(c)(d)
$\phi = 0.074$	280	Gardner, Wijayaratne, and Calvert, 1984[3]	(f)
$\phi = 0.080$	290		
$\phi = 0.076$	299		
$\phi = 0.074$	313		
$\phi_1 = 0.76$	250	Meyrahn *et al.*, 1986[2]	(g)
$\phi_1 = 0.80$	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) Graphical presentation of ϵ/dm^3 mol^{-1} cm^{-1} (base 10) vs wavelength at 298 K. Spectrum determined in a 10 cm path length over a range of pressures of CH_3COCH_3 at an undefined spectral resolution length.

(b) Absorption cross sections measured from 250 to 360 nm in cells of 0.1 and 1 m path length, with a resolution of 0.04 nm at half-width. The tabulated cross sections were derived by averaging the high-resolution data over 3 nm wavelength intervals.

(c) Review of earlier work on the photolysis of acetone vapor alone by Noyes *et al.*,[4] Heicklen and Noyes,[5] Heicklen,[6] Ausloos and Murad,[7] and Doepker and Mains.[8]

(d) Measured at 298 K.

(e) Measured above 373 K.

(f) Study of the quantum yields of acetone loss and formation of products CO_2, CO, CH_3OH, and CH_2O in the photolysis of dilute mixtures of acetone ($\sim$0.36 Torr) in air (25–745 Torr) over temperature range 272–301 K. Quantum yields for acetone loss and formation of CO_2 were equal, and listed values of ϕ are averaged data for 298 K, which were taken as a measure of the extent of photodissociation of acetone.

(g) Study of the quantum yields of formation of CO_2 and CO in the photolysis of dilute mixtures of acetone (0.1–0.15 Torr) in air (753 Torr) at room temperature. In addition the quantum yields of formation of peroxyacetyl–nitrate (PAN) were measured when trace amounts of NO_2 (9.1×10^{-5} Torr) 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

Wavelength/nm	$10^{20}\sigma/cm^2$	ϕ_1	ϕ_2
250	2.37	0.76	
260	3.66	0.80	
270	4.63	0.64	
280	5.05	0.55	
290	4.21	0.30	
300	2.78	0.15	
310	1.44	0.05	
320	0.48	0.028	
330	0.08	0.033	
340	0.01		
350	0.003		

Comments on Preferred Values

The preferred absorption cross sections, which are those measured by Meyrahn *et al.*,[2] are in substantial agreement with the absorption spectrum reported by Calvert and Pitts.[1]

The two recent studies,[2,3] of the photodissociation of acetone in air are not in agreement regarding the quantum yield measurements. As pointed out by Meyrahn *et al.*[2] further work is required on this system 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.*[2] on the basis that the trend in ϕ_1 with varying wavelength observed by these authors appears to be more reasonable.

References

[1] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).

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[5] J. Heicklen and W. A. Noyes, J. Am. Chem. Soc. **81**, 3858 (1959).

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[8] R. D. Doepker and G. J. Mains, J. Am. Chem. Soc. **83**, 294 (1961).

$CH_3CO_3NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reactions		ΔH°_{298}/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CO_3NO_2 + h\nu \rightarrow CH_3CO_3 + NO_2$	(1)		
$\rightarrow CH_3CO_2 + NO_3$	(2)		

Absorption cross section data

Wavelength range/nm	Reference	Comments
200–300	Senum, Lee, and Gaffney, 1984[1]	(a)
210–250	Basco and Parmar, 1987[2]	(b)

Comments

(a) Measured at 298 K in a 10.1 cm cell with a spectral resolution of 2 nm, and over the pressure range 2.5 to 25 Torr of PAN. Cross sections at $\lambda > 300$ nm were not recorded since the light absorption was negligible in this region under these experimental conditions.

(b) Derived from measurements following the flash photolysis of mixtures of Cl_2, CH_3CHO, O_2, N_2, and NO_2 at total pressures of 76–612 Torr. The absorption spectrum of PAN was obtained from the total residual absorption 10 s to 2 min after the photoflash using a xenon lamp as a monitoring source.

Preferred Values

Absorption cross sections

Wavelength/nm	$10^{20}\sigma/cm^2$	Wavelength/nm	$10^{20}\sigma/cm^2$
200	317	255	7.9
205	237	260	5.7
210	165	265	4.04
215	115	270	2.79
220	77	275	1.82
225	55	280	1.14
230	39.9	285	0.716
235	29.0	290	0.414
240	20.9	295	0.221
245	15.0	300	0.105
250	10.9		

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values of the absorption cross sections are those reported by Senum, Lee, and Gaffney,[1] which are in substantial agreement with the previously recommended provisional data, and with the less direct measurements of Basco and Parmar.[2]

Measurements are still needed on the quantum yields and relative importance of the proposed primary processes. In the meantime it is again suggested that it be assumed that $\phi_1 + \phi_2 = 1$ for absorption in the UV region, by analogy with other organic nitrates.

Channel (1) forming CH_3CO_3 and NO_2 would appear to be the more likely photochemical primary process.

References

[1]G. I. Senum, Y.-N. Lee, and J. S. Gaffney, J. Phys. Chem. **88**, 1269 (1984).

[2]N. Basco and S. S. Parmer, Int. J. Chem. Kinet. **19**, 115 (1987).

[3]CODATA Supplement I, 1982 (see References in Introduction).

4.5. Sulfur Species

$HO + H_2S \rightarrow H_2O + HS$

$\Delta H^\circ = -120$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.6\times10^{-12}\exp(-57/T)$	245–450	Lin *et al.*, 1985[1]	(a)
$(4.4\pm0.7)\times10^{-12}$	299		
$1.32\times10^{-11}\exp[(-394\pm190)/T]$	294–463	Lafage *et al.*, 1987[2]	(b)
$(3.3\pm0.5)\times10^{-12}$	294		
Relative Rate Coefficients			
$(5.5\pm0.8)\times10^{-12}$	300	Barnes *et al.*, 1986[3]	(c)
Reviews and Evaluations			
$6.3\times10^{-12}\exp(-80/T)$	200–300	CODATA 1984[4]	(d)
$5.9\times10^{-12}\exp(\ 65/T)$	200–300	NASA, 1985[5]	(c)
$5.9\times10^{-12}\exp(-70/T)$	200–300	NASA 1987[6]	(f)

Comments

(a) Discharge–flow study, He carrier gas. HO produced by $H + NO_2$ reaction. Passage of H_2/He mixture through a microwave discharge or over a heated filament used as sources of H. [HO] monitored by resonance fluorescence at 309 nm. Changes in pressure and use of N_2 or O_2 as carrier gases have no effect on k.

(b) Discharge–flow study; He carrier gas. HO produced by $H + NO_2$ reaction. NO_2 in excess scavenges any HS radicals produced. [HO] monitored by laser-induced fluorescence or resonance fluorescence. Minimum in plot of k vs T observed; minimum value of $k = (33\pm5)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(c) HO radicals produced by photolysis of CH_3ONO/O_2 mixture in air at 1 atm pressure in 38 ℓ reaction vessel.

Removal of H_2S relative to reference hydrocarbon measured by gas chromatography. $k/k(HO + C_2H_4) = 0.65 \pm 0.10$. k obtained using $k(HO + C_2H_4) = 8.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(d) Based on results of Wine *et al.*,[7] Leu and Smith,[8] Michael *et al.*,[9] Lin,[10] Westenberg and de Haas,[11] and Perry *et al.*[12]

(e) Based on references cited in (c) plus Cox and Sheppard.[13]

(f) Based on references cited in (e) plus Barnes *et al.*[2]

Preferred Values

$k = 4.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.3 \times 10^{-12} \exp(-80/T)$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

$\Delta (E/R) = \pm 80$ K.

Comments on Preferred Values

The most recent studies are in excellent agreement with previous work. Both Lin *et al.*[1] and Lafage *et al.*[2] confirm the finding of Leu *et al.*[8] that k exhibits non-Arrhenius behavior over the range 245–450 K the Arrhenius plot appearing to have a shallow minimum at approximately 270–300 K, and also in agreement with Leu *et al.*,[8] Lin *et al.*[1] find that the value of k appears to be independent of pressure and nature of the bath gas. These latter results throw some doubt upon the suggestion that the non-Arrhenius behavior is due to the occurrence of both addition and abstract channels.

Despite the non-Arrhenius behavior of k over an extended temperature range, the preferred expression is given in Arrhenius from, which is satisfactory for the limited temperature range covered by our recommendations.

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$HO + CH_3SH \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.89 \times 10^{-12} \exp[(398 \pm 151)/T]$	300–423	Atkinson, Perry, and Pitts, 1977[1]	(a)
$(3.39 \pm 0.34) \times 10^{-11}$	300		
$(1.15 \pm 0.39) \times 10^{-11} \exp[(338 \pm 100)/T]$	244–366	Wine *et al.*, 1981[2]	(a)
$(3.37 \pm 0.41) \times 10^{-11}$	298		
$(2.1 \pm 0.2) \times 10^{-11}$	293	Mac Leod, Poulet, and Le Bras, 1983[3]; Mac Leod *et al.*, 1984	(b)
$(2.56 \pm 0.44) \times 10^{-11}$	296	Lee and Tang, 1983[5]	(c)
$(1.01 \pm 0.19) \times 10^{-11} \exp[(347 \pm 59)/T]$	254–430	Wine, Thompson, and Semmes, 1984[6]	(a)
3.24×10^{-11}	298		
3.17×10^{-11}	300	Hynes and Wine, 1987[7]	(d)
Relative Rate Coefficients			
$(9.7 = 0.9) \times 10^{-11}$	297	Cox and Sheppard, 1980[8]	(e)
$(3.7 \pm 0.4) \times 10^{-11}$	300	Barnes *et al.*, 1986[9]	(f)
Reviews and Evaluations			
$9.70 \times 10^{-12} \exp(366/T)$	244–430	Atkinson, 1986[10]	(g)

Comments

(a) Flash photolysis–resonance fluorescence detection of HO.

(b) Discharge flow–electron paramagnetic resonance detection of HO.

(c) Discharge flow–resonance fluorescence detection of HO.

(d) Laser photolysis–laser-induced fluorescence detection of HO. The rate coefficient was observed to be independent of total pressure and of the presence or absence of O_2, up to 700 Torr total pressure of O_2. Experiments were also carried out at 270 K, yielding a rate coefficient of 3.69×10^{-11} cm^3 molecule^{-1} s^{-1}.

(e) Relative rate method. HO radicals generated by photolysis of HONO–NO–air mixtures at atmospheric pressure. Decay rate of CH_3SH measured relative to that of C_2H_4, and the relative rate coefficient placed on an absolute basis by use of $k(\mathrm{HO} + \mathrm{C_2H_4}) = 8.58 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[10]

(f) Relative rate method. HO radicals generated by photolysis of H_2O_2 in N_2 at atmospheric pressure. Decay rate of CH_3SH measured relative to that for propene, and the relative rate coefficient placed on an absolute basis by use of $k(\mathrm{HO} + \text{propene}) = 2.60 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[10]

(g) Derived from a least-squares analysis of the absolute flash photolysis–resonance fluorescence data of Atkinson *et al.*[1] and Wine *et al.*,[2,6] which are in excellent agreement.

Preferred Values

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

$k = 9.9 \times 10^{-12} \exp(356/T)$ cm^3 molecule^{-1} s^{-1} over the range 240–430 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are based upon a least-squares analysis of the absolute rate coefficients of Atkinson *et al.*,[1] Wine *et al.*,[2,6] and Hynes and Wine,[7] which are in excellent agreement. The recent relative rate study of Barnes *et al.*[9] shows that erroneous rate coefficient data are obtained in the presence of O_2 and NO, thus accounting for the much higher value of Cox and Sheppard.[8] The study of Hynes and Wine[7] shows that there is no observable effect of O_2 on the measured rate coefficient. The reaction proceeds via initial addition of HO to form the adduct $CH_3S(OH)H$,[6] which is sufficiently thermally stable over the temperature range studied to date not to dissociate back to products over the time scale of the measurements.

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$\mathrm{HO + CH_3SCH_3 \rightarrow H_2O + CH_2SCH_3}$ (1)
$\mathrm{\rightarrow CH_3S(OH)CH_3}$ (2)

$\Delta H^\circ = -94.9$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_1 = (3.80 \pm 0.30) \times 10^{-12}$	273	Martin, Jourdain, and Le Bras, 1985[1]	(a)
$k_1 = (3.22 \pm 0.16) \times 10^{-12}$	293		
$k_1 = (3.66 \pm 0.19) \times 10^{-12}$	318		
$k_1 = (2.5^{+0.9}_{-0.6}) \times 10^{-12} \exp[(130 \pm 102)/T]$	297–400	Wallington *et al.*, 1986[2]	(b)
$k_1 = (3.6 \pm 0.2) \times 10^{-12}$	297		
$k_1 = (1.36 \pm 0.40) \times 10^{-11} \exp[-(332 \pm 96)/T]$	276–397	Hynes, Wine, and Semmes, 1986[3]	(b)
$k_1 = 4.46 \times 10^{-12}$	298		
$k = (6.28 \pm 0.10) \times 10^{-12}$ (1 atm of air)	298	Hynes, Wine, and Semmes, 1986[3]	(c)
$k_1 = (1.18 \pm 0.22) \times 10^{-11} \exp[-(236 \pm 150)/T]$	260–393	Hsu, Chen, and Lee, 1987[4]	(d)
$k_1 = (5.5 \pm 1.0) \times 10^{-12}$	298		
Relative Rate Coefficients			
$k = (9.7 \pm 1.0) \times 10^{-12}$ (1 atm of air)	296	Atkinson, Pitts, and Aschmann, 1984[5]	(e)
$k = 7.8 \times 10^{-12}$	298	CODATA, 1984[6]	(f)
$k_1 = 6.78 \times 10^{-12} \exp(-137/T)$	248-363	Atkinson, 1986[7]	(g)
$k = (4.28 + 3.82 \times 10^{-19}[O_2]) \times 10^{-12}$	298		

Comments

(a) Discharge flow–electron paramagnetic resonance detection of HO.

(b) Flash photolysis–resonance fluorescence detection of HO.

(c) Laser photolysis–laser induced fluorescence detection of HO, with the effect of O_2 being investigated over the temperature range 261–321 K. The measured rate coefficient was observed to depend linearly on the O_2 concentration, and the rate coefficient given in the table is that measured at 750 Torr total pressure of air. The rate coefficient measured in the absence of O_2 is ascribed to reaction step (1), with the adduct formed in step (2) rapidly dissociating back to the reactants. In the presence of O_2 this adduct reacts rapidly with O_2, and hence the measured rate coefficient increases with the O_2 concentration.

(d) Discharge flow–resonance fluorescence detection of HO. Rate coefficient was not affected by the addition of up to 1 Torr of O_2.

(e) Relative rate method. HO radicals generated by photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. Decay of CH_3SCH_3 monitored relative to *n*-hexane, and the relative rate coefficient placed on an absolute basis by use of $k(\text{HO} + n\text{-hexane}) = 5.53\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[7]

(f) Derived from the mean of the room-temperature rate coefficients of Kurylo,[8] Atkinson *et al.*,[9] Cox, and Sheppard[10] and Wine *et al.*[11]

(g) The recommended rate coefficient in the absence of O_2 was that of Wine *et al.*[11] and was ascribed to the H-atom abstraction pathway. The as-then-unpublished data of Hynes *et al.*[3] were used to recommend the rate coefficient at 298 K as a function of the O_2 concentration (due to a typographical error, this was given incorrectly), with a rate coefficient at 760 Torr, total pressure of air of 6.3×10^{-12} cm^3 molecule^{-1} s^{-1} being recommended.

Preferred Values

$$k = 4.4\times10^{-12} + \left[\frac{4.1\times10^{-31}[O_2]}{(1 + 4.1\times10^{-20}[O_2])}\right] \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}$$

$k_1 = 4.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 9.6\times10^{-12} \exp(-234/T)$ over the range 250–400 K.

$k_2 = 4.1\times10^{-31}[O_2]/(1 + 4.1\times10^{-20}[O_2])$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2 = 1.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 atm total pressure of air.

$k_2 = 1.7\times10^{-42} \exp(7810/T)[O_2]/(1 + 5.5\times10^{-31} \exp(7460/T)[O_2])$ cm^3 molecule^{-1} s^{-1} over the range 260–360 K.

Reliability

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

$\Delta (E_1/R) = \pm 300$ K.

$\Delta \log k_2 = \pm 0.3$ at 298 K and 1 atm of air.

Comments on Preferred Values

It is now recognized[3,7] that this reaction proceeds via the two reaction steps (1) and (2). The $CH_3S(OH)CH_3$ adduct radical decomposes sufficiently rapidly so that in the absence of O_2 only the rate coefficient k_1 is measured. In the presence of O_2, the $CH_3S(OH)CH_3$ radical reacts by

$$CH_3S(OH)CH_3 + O_2 \rightarrow \text{products.}$$

Hence, only in the presence of O_2 is the addition channel (2) observed, with the observed rate constant being dependent on the O_2 concentration (but, to at least a first approximation, not on the concentration of other third bodies such as N_2, Ar, SF_6).[3]

The relative rate study of Wallington *et al.*[2] shows that previous relative rate studies were complicated by secondary reactions, and that all relative rate coefficient studies carried out in the presence of NO are of dubious quality. The most recent absolute rate coefficients measured in the absence of O_2[1-4] agree that the earliest absolute rate coefficients of Atkinsonn *et al.*[8] and Kurylo[9] are erroneously high, and those of Mac Leod *et al.*[10] were in error owing to heterogeneous wall reactions.[1] The preferred rate coefficient k_1 for the H-atom abstraction channel is based upon the two studies of Wine and co-workers,[3,11] and the rate coefficient for the HO radical addition channel (step 2) utilizes the recent data of Hynes *et al.*[3] While the expression for k_2 is strictly valid only for 700 Torr total pressure of air[3] (in that the rate coefficients for HO addition to CH_3SCH_3 and the reverse dissociation step may be in the falloff regime), this equation fits the room-temperature data obtained at pressures of air from 50 to 750 Torr well.

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$HO + CS_2 \rightarrow$ products

Comments

Wine *et al.* have studied this reaction by pulsed laser photolysis of H_2O_2 at 248 nm in mixtures of CS_2 with added He, N_2, air, and O_2. [HO] was monitored by laser-induced fluorescence.

The results confirm that the rate of reaction is extremely slow in the absence of O_2. In the presence of O_2 the rate is rapid and is consistent with the mechanism.

$$HO + CS_2 + M \rightleftarrows HOCS_2 + M.$$

$$HOCS_2 + O_2 \rightarrow \text{products.}$$

In the presence of air at 1 atm the effective rate constant obtained by Wine *et al.*[1] is given by $k = 6.9\times10^{-14} \exp(1150/T)$ cm^3 molecule^{-1} s^{-1}. This expression gives values 25%–50% higher than our previously recommended values,[2] and the temperature coefficient differs significantly from that obtained by Barnes *et al.*[3] and Ravishankara *et al.*[4]

Our recommendations are unchanged, but it is clear that the reaction is quantitatively far from being understood.

References

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$HO + OCS \rightarrow$ products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.13 \times 10^{-13} \exp(-1200/T)$	255–483	Cheng and Lee, 1986[1]	(a)
$(2.0^{+0.4}_{-0.8}) \times 10^{-15}$	300		
$(1.92 \pm 0.25) \times 10^{-15}$	298	Wahner and Ravishankara, 1987[2]	(b)
Reviews and Evaluations			
$1.3 \times 10^{-12} \exp(-2300/T)$	200–520	CODATA, 1984[3]	(c)
$3.9 \times 10^{-13} \exp(-1780/T)$	200–300	NASA, 1985[4]	(d)
$1.1 \times 10^{-13} \exp(-1200/T)$	200–300	NASA, 1987[5]	(e)

Comments

(a) Discharge–flow study, He carrier gas. HO generated by $H + NO_2$ reaction; excess NO_2 used to ensure removal of H atoms that may lead to complicating side reactions. Purity of OCS checked by FTIR; H_2S present at less than 0.005%. [HO] monitored by resonance fluorescence at 309 nm. k independent of pressure (0.9–5.9 Torr) and addition of O_2 (up to 18%).

(b) Laser pulse photolysis using a variety of HO sources (H_2O_2, HNO_3, HONO). Xe flash lamp used in some experiments. [HO] monitored by laser-induced fluorescence. Value of k independent of pressure (90–300 Torr), nature of buffer gas, and O_2 addition (up to 36 Torr).

(c) Based on results of Leu and Smith.[6]

(d) Based on results of Leu and Smith[6] and Friedl *et al.*[7]

(e) Based on results of Cheng and Lee[1] and Wahner and Ravishankara.[2]

Preferred Values

$k = 2.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.1 \times 10^{-13} \exp(-1200/T)$ cm^3 molecule^{-1} s^{-1} over range 250–500 K.

Reliability

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

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

Comments on Preferred Values

Values of k measured recently by Cheng and Lee[1] and by Wahner and Ravishankara[2] are approximately a factor of 3 lower at 298 K than the previously recommended value of Leu and Smith.[6] It has been suggested that this may be due to the corrections applied by Leu and Smith to allow for the presence of traces of H_2S in their system since in the absence of such corrections there is reasonable agreement between the studies. Cheng and Lee took care to keep the H_2S level in their OCS very low and this, together with the confirmatory measurements of Wahner and Ravishankara, leads us to recommend their values.

References

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$HO + SO_2 + M \rightarrow HOSO_2 + M$

$\Delta H^\circ = -128$ kJ mol^{-1}

Comment

The recent discharge–flow EPR study of this reaction at a pressure of 6.4 Torr of He and at 298 K by Martin, Jourdain, and Le Bras[1] gave results close to the low-pressure limit that are in good agreement with our earlier recommendation.[2] The study by Barnes *et al.*[3] confirms these results. A discussion of the heat of reaction was given in Ref. 4. The apparent differences in the recommended low- and high-pressure rate coefficients between our earlier evaluation[2] and the NASA evaluation[5] are due to the use of a lower $F_c = 0.45$ in the former case (following Ref. 6) and the use of a standard $F_c = 0.6$ in the latter work.

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$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$

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

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.0 \pm 2) \times 10^{-13}$	250	Margitan, 1984[1]	(a)
$(4.0 \pm 2) \times 10^{-13}$	298		
$(3.5 \pm 1) \times 10^{-13}$	298	Martin, Jourdain, and Le Bras, 1986[2]	(b)
$(4.37 \pm 0.66) \times 10^{-13}$	298	Gleason, Sinha, and Howard, 1987[3]	(c)
Reviews and Evaluations			
4.0×10^{-13}	298	NASA, 1985[4]	(d)
$1.3 \times 10^{-12} \exp(-330/T)$	200–300	NASA, 1987[5]	(e)

Comments

(a) Pulsed laser photolysis of $HNO_3/Ar/SO_2$ mixtures at 226 nm. [HO] monitored by resonance fluorescence. System studied at 40 and 100 Torr. Ar and at 250 and 298 K. HO removed by $HO + SO_2 + M \rightarrow HOSO_2 + M$ but addition of O_2 and NO regenerates HO by $HOSO_2 + O_2 \rightarrow HO_2 + SO_3$, $HO_2 + NO \rightarrow HO + NO_2$. Effects of varying amounts of O_2 studied. Same value of k found at 250 K and 298 K, but author suggests that his is due to lack of precision in the technique rather than indicating the k is temperature independent.

(b) Discharge–flow study of reaction $HO + SO_2 + M \rightarrow HOSO_2 + M$. [HO] produced by $H + NO_2$ reaction in He carrier gas. [HO] monitored by esr, calibrated with NO. Effects of addition of NO and O_2 on [HO] decay studied. System of 12 reactions used to model system to obtain k.

(c) Discharge–flow system, N_2 carrier gas. HO produced by $H + NO_2$ reaction. SO_2 and O_2 added downstream. [$HOSO_2$] monitored by sampling into a flowing afterglow containing Cl^- ions. SO_3^-, formed by $Cl^- + HOSO_2 \rightarrow SO_3^- HCl$, detected by quadrupole mass spectrometry. SO_3 product of the reaction also detected by $Cl^- + SO_3 + M \rightarrow (ClSO_3)^- + M$ and mass spectrometric measurement of $(ClSO_3)^-$. Pressure varied over range 2–8 Torr, no change in k observed putting limit of 3.4×10^{-31} cm^6 $molecule^{-2}$ s^{-1} ($M = N_2$) on rate constant for $HOSO_2 + O_2 + M \rightarrow HOSO_2O_2 + M$.

(d) Accepts value of Margitan.[1]

(e) Based on work of Gleason *et al.*,[3] and unpublished work of Gleason and Howard and Bando and Howard.

Preferred Values

$k = 4.0 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The earlier studies of this reaction were based on the effects of O_2/NO mixtures on the rate of HO removal by the reaction $HO + SO_2 + M \rightarrow HOSO_2 + M$. The inevitable occurrence of other reactions in these systems limited the precision with which k could be determined. The recent work of Gleason *et al.* in which [$HOSO_2$] was monitored is much more direct, more precise, and gives a value of k at 298 K confirming the earlier less precise measurements.

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$NO_3 + H_2S \rightarrow$ products

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leqslant 3 \times 10^{-14}$	298	Wallington *et al.*, 1986[1]	(a)
$< 8 \times 10^{-16}$	298	Dlugokencky and Howard, 1988[2]	(b)
Relative Rate Coefficients			
$< 2 \times 10^{-14}$	298	Cantrell *et al.*, 1987[3]	(c)
Reviews and Evaluations			
$< 3.0 \times 10^{-14}$	298	NASA, 1987[4]	(d)

Comments

(a) Flash photolysis–optical absorption detection of NO_3.

(b) Flow system–laser-induced fluorescence detection of NO_3.

(c) Relative rate method. NO_3 generated by the thermal decomposition of N_2O_5, rate coefficient placed on an absolute basis by use of an equilibrium constant for the $NO_3 + NO_2 \rightleftarrows N_2O_5$ reactions of 2.3×10^{-11} cm^3 molecule^{-1}.

(d) Based upon the upper limit to the rate coefficient determined by Wallington *et al.*[1]

Preferred Values

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

Comments on Preferred Values

The preferred upper limit to the rate coefficient is based upon the study of Dlugokencky and Howard.[2]

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$NO_3 + CS_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<4 \times 10^{-16}$	298	Burrows, Tyndall, and Moortgat, 1985[1]	(a)
Relative Rate Coefficients			
$<4.8 \times 10^{-14}$	297	Mac Leod *et al.*, 1986[2]	(b)

Comments

(a) Molecular modulation system–optical absorption detection of NO_3.

(b) Relative rate method. NO_3 generated by thermal decomposition of N_2O_5 at atmospheric pressure of air. Decay rates of CS_2 and *trans*-2-butene monitored by FT–IR absorption spectroscopy. Upper limit to the rate coefficient obtained by use of $k(NO_3 + trans\text{-2-butene}) = (3.87 \pm 0.45) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[3,4]

Preferred Values

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

Comments on Preferred Values

The preferred value is based upon the absolute study of Burrows *et al.*,[1] which is consistent with the higher upper limit derived by Mac Leod *et al.*[2]

References

[1] J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, J. Phys. Chem. **89**, 4848 (1985).
[2] H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).
[3] A. R. Ravishankara and R. L. Mauldin III, J. Phys. Chem. **89**, 3144 (1985).
[4] E. Dlugokencky and C. J. Howard, J. Phys. Chem. **93**, 1091 (1989).

$NO_3 + COS \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$<2.1 \times 10^{-15}$	297	Mac Leod *et al.*, 1986[1]	(a)

Comments

(a) Relative rate method. NO_3 radicals generated by the thermal decomposition of N_2O_5 at atmospheric pressure of air. Decay rates of COS and *trans*-2-butene monitored by FT–IR absorption spectroscopy. Upper limit to the rate coefficient obtained by use of $k(NO_3 + trans\text{-2-butene}) = (3.87 \pm 0.45) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[2,3]

Preferred Values

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

Comments on Preferred Values

The preferred value is based upon the sole study of Mac Leod *et al.*,[1] with a somewhat higher upper limit than reported.

References

[1] H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).
[2] A. R. Ravishankara and R. L. Mauldin III, J. Phys. Chem. **89**, 3144 (1985).
[3] E. Dlugokencky and C. J. Howard, J. Phys. Chem. **93**, 1091 (1989).

$NO_3 + SO_2 \rightarrow$ products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$< 4 \times 10^{-16}$	298	Burrows, Tyndall, and Moortgat, 1985[1]	(a)
$\leqslant 4 \times 10^{-16}$	298	Wallington *et al.*, 1986[2]	(b)
$< 1 \times 10^{-15}$	298	Dlugokencky and Howard, 1988[3]	(c)
Relative Rate Coefficients			
$< 7 \times 10^{-21}$	303	Daubendiek and Calvert, 1975[4]	(d)
Reviews and Evaluations			
$< 7.0 \times 10^{-21}$	298	NASA, 1987[5]	(e)

Comments

(a) Molecular modulation system–optical absorption detection of NO_3.

(b) Flash photolysis–optical absorption detection of NO_3.

(c) Flow system–laser-induced fluorescence detection of NO_3.

(d) Relative rate method. NO_3 radicals generated by thermal decomposition of N_2O_5.

(e) Based upon the study of Daubendiek and Calvert.[4]

Preferred Values

$k < 1 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based upon the relative rate study of Daubendiek and Calvert,[4] with a much higher upper limit.

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**, 5393 (1986).
[3] E. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).
[4] R. L. Daubendiek and J. G. Calvert, Environ. Lett. **8**, 103 (1975).
[5] NASA Evaluation No. 8, 1987 (see References in Introduction).

$NO_3 + CH_3SH \rightarrow$ Products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.0^{+2.6}_{-0.7}) \times 10^{-13} \exp[(600 \pm 400)/T]$	280–350	Wallington *et al.*, 1986[1]	(a)
$(8.1 \pm 0.6) \times 10^{-13}$	298		
$(7.7 \pm 0.5) \times 10^{-13}$	298	Rahman *et al.*, 1988[2]	(b)
$(1.09 \pm 0.17) \times 10^{-12} \exp[(0 \pm 50)/T]$	254–367	Dlugokencky and Howard, 1988[3]	(c)
$(1.09 \pm 0.13) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(9.9 \pm 2.2) \times 10^{-13}$	297	Mac Leod *et al.*, 1986[4]	(d)

Comments

(a) Flash photolysis–optical absorption spectroscopic detection of NO_3. Carried out at total pressures of 50–100 Torr of N_2.

(b) Discharge flow–mass spectrometric detection of CH_3SH in the presence of excess concentrations of NO_3 radicals. Carried out at total pressures of ~1 Torr. Corrections were made for the reaction of the CH_3SH with the F_2 used as the precursor to generate NO_3 radicals.

(c) Flow system with laser-induced fluorescence detection of NO_3. Carried out at total pressures of ~1 Torr.

(d) Relative rate method. NO_3 radicals generated by the thermal decomposition of N_2O_5 in N_2O_5–NO_2–air mixtures at atmospheric pressure. Decay rates of CH_3SH and *trans*-2-butene monitored, and the rate coefficient placed on an absolute basis by use of $k(NO_3 + trans\text{-2-butene}) = 3.87 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[5,6]

Preferred Values

$k = 9.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–370 K.

Reliability

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

$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Value

The preferred value at 298 K is the mean of the four studies carried out to date,[1-4] which are in reasonably good agreement. Although a significant negative temperature dependence is indicated by the absolute rate coefficient study of Wallington *et al.*,[1] this is due to the rate coefficient measured at 350 K, since the rate coefficients at 280 and 298 K are identical.[1] The temperature independence determined by Dlugokencky and Howard[3] is accepted. The experimental data indicate that there is no pressure dependence of the rate coefficient, at least over the range ~1–700 Torr.

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).

[2] M. M. Rahman, E. Becker, Th. Benter, and R. N. Schindler, Ber. Bunsenges Phys. Chem. **92**, 91 (1988).

[3] E. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).

[4] H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).

[5] A. R. Ravishankara and R. L. Mauldin III, J. Phys. Chem. **89**, 3144 (1985).

[6] E. Dlugokencky and C. J. Howard, J. Phys. Chem. **93**, 1091 (1989).

$NO_3 + CH_3SCH_3 \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.5 \pm 0.5) \times 10^{-13}$	298	Wallington *et al.*, 1986[1]	(a)
$(4.7^{+2.6}_{-1.7}) \times 10^{-13} \exp[(170 \pm 130)/T]$	280–350	Wallington *et al.*, 1986[2]	(a)
$(8.1 \pm 1.3) \times 10^{-13}$	298		
$(1.0 \pm 0.2) \times 10^{-12}$	278–318	Tyndall *et al.*, 1986[3]	(b)
$(1.79 \pm 0.22) \times 10^{-13} \exp[(530 \pm 40)/T]$	256–376	Dlugokencky and Howard, 1988[4]	(c)
$(1.06 \pm 0.13) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(9.9 \pm 0.2) \times 10^{-13}$	296	Atkinson. Pitts. and Aschmann. 1984[5]	(d)

Comments

(a) Flash photolysis–optical absorption spectrometric detection of NO_3. Carried out at total pressures of 50–400 Torr of He[1] or 50–100 Torr of N_2.[2]

(b) Molecular modulation technique, with optical absorption detection of NO_3. Carried out at total pressures of 20 Torr of N_2.

(c) Flow system with laser-induced fluorescence detection of NO_3. Carried out at total pressures of ~1 Torr.

(d) Relative rate method. NO_3 radicals generated by thermal decomposition of N_2O_5 in NO_2–air mixtures at atmospheric pressure. Relative decay rates of CH_3SCH_3 and *trans*-2-butene measured, and the rate coefficient placed on an absolute basis by use of $k(NO_3 + trans\text{-2-butene}) = 3.87 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[6,7]

Preferred Values

$k = 1.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.9 \times 10^{-13} \exp(500/T)$ cm^3 molecule^{-1} s^{-1} over the range 250–380 K.

Reliability

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

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

Comments on Preferred Values

The absolute[1-4] and relative[5] rate coefficient studies are in good agreement, although the data of Wallington *et al.*[1,2] are ~20% lower than the other sets of data.[3-5] The 298 K preferred value is based mainly on the rate coefficients measured by Tyndall *et al.*,[3] Dlugokencky and Howard[4] and Atkinson *et al.*[5] The temperature dependence is taken from the study of Dlugokencky and Howard.[5] The study of Tyndall *et al.*[3] was carried out over a narrow temperature range such that the data obtained are consistent with the temperature dependence of Dlugokencky and Howard.[4] The experimental data show that the rate coefficient is independent of total pressure over the range ~1–740 Torr.

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 4640 (1986).

[2] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).

[3] G. S. Tyndall, J. P. Burrows, W. Schneider, and G. K. Moortgat, Chem. Phys. Lett. **130**, 463 (1986).

[4] E. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).

[5] R. Atkinson, J. N. Pitts, Jr., and S. M. Aschmann, J. Phys. Chem. **88**, 1584 (1984).

[6] A. R. Ravishankara and R. L. Mauldin III, J. Phys. Chem. **89**, 3144 (1985).

[7] E. Dlugokencky and C. J. Howard, J. Phys. Chem. **93**, 1091 (1989).

$NO_3 + CH_3SSCH_3 \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.9 \pm 0.3) \times 10^{-13} \exp[(290 \pm 50)/T]$	280–350	Wallington *et al.*, 1986[1]	(a)
$(4.9 \pm 0.8) \times 10^{-13}$	298		
$(7.4 \pm 1.5) \times 10^{-13} \exp[(0 \pm 200)/T]$	334–382	Dlugokencky and Howard, 1988[2]	(b)
$(7.4 \pm 1.5) \times 10^{-13}$	298*		
Relative Rate Coefficients			
$(4.3 \pm 0.8) \times 10^{-14}$	297	Mac Leod *et al.*, 1986[3]	(c)

Comments

(a) Flash photolysis–optical absorption detection of NO_3 at total pressures of 50–100 Torr of N_2.

(b) Flow system with laser-induced fluorescence detection of NO_3 at total pressures of ~1 Torr.

(c) Relative rate method. NO_3 radicals generated by thermal decomposition of N_2O_5 in N_2O_5–NO_2–air mixtures at atmospheric pressure. Relative decay rates of CH_3SSCH_3 and *trans*-2-butene monitored, and the relative rate coefficient placed on an absolute basis by use of $k(NO_3 + trans\text{-}2\text{-butene}) = 3.87 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[4,5] A more recent study[6] has shown that reliable rate coefficient data cannot be obtained from the chemical system used.

Preferred Values

$k = 7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range ~300–380 K.

Reliability

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

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

Comments on Preferred Value

The two absolute studies[1,2] are in reasonable agreement with respect to the room-temperature rate coefficient. While the reported rate coefficient from the relative rate study[3] is an order of magnitude lower than the absolute data, the recent study of Atkinson *et al.*[6] shows that this is due to complexities in the experimental system used. Accordingly, the preferred values are based upon the absolute rate studies, and then mainly on the most recent data of Dlugokencky and Howard,[2] with the error limits being sufficient to encompass the data of Wallington *et al.*[1]

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).

[2] E. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).

[3] H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).

[4] A. R. Ravishankara and R. L. Mauldin III, J. Phys. Chem. **89**, 3144 (1985).

[5] E. Dlugokencky and C. J. Howard, J. Phys. Chem. **93**, 1091 (1989).

[6] R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., J. Geophys. Res. **93**, 7125 (1988).

$HS + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<4\times10^{-17}$	298	Black 1984[1]	(a)
$<1\times10^{-17}$	298	Friedl, Brune, and Anderson, 1985[2]	(b)
$<1\times10^{-14}$	298	Schoenle, Rahman, and Schindler, 1987[3]	(c)
$<4\times10^{-19}$	298	Stachnik and Molina, 1987[4]	(d)
$<1.5\times10^{-17}$	295	Wang, Lovejoy, and Howard, 1987[5]	(e)
Reviews and Evaluations			
$<3\times10^{-15}$	298	CODATA, 1984[6]	(f)
$<1.0\times10^{-17}$	298	NASA, 1985[7]	(g)
$<4\times10^{-19}$	298	NASA, 1987[8]	(h)

Comments

(a) Pulsed laser photolysis of H_2S at 193 nm. [HS] monitored by laser-induced fluorescence. No observable decay of HS in 500 Torr O_2.

(b) Discharge–flow study, He carrier gas. HS generated by $H + H_2S$ reaction. [HS] monitored by laser-induced fluorescence.

(c) Discharge–flow study, He carrier gas. HS generated by $F + H_2S$ reaction, [HS] monitored by mass spectrometry.

(d) Pulsed laser photolysis of H_2S at 193 nm. [HS] monitored by absorption at 324 nm using multipass cell. Sufficient CO added to scavenge HO, $CO + HO \rightarrow CO_2 + H$.

(e) Discharge–flow study, He carrier gas. HS generated by $F + H_2S$ or $H + C_2H_4S$. [HS] monitored by laser magnetic resonance.

(f) Accepts upper limit of Tiee *et al.*[8]

(g) Accepts upper limit of Friedl *et al.*[2]

(h) Accepts upper limit of Stachnik and Molina.[4]

Preferred Values

$k \leqslant 4\times10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The reaction of HS with O_2 is so slow that attempts to measure the rate coefficient have yielded only upper limits that fall in the range 4×10^{-19}–10^{-17} cm^3 molecule^{-1} s^{-1}. The preferred value is from the study of Stachnik and Molina,[4] which is particularly sensitive and seems soundly conceived and executed.

References

[1] G. Black, J. Chem. Phys. **80**, 1103 (1984).
[2] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1987).
[3] G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **91**, 66 (1987).
[4] R. A. Stachnik and M. J. Molina, J. Phys. Chem. **91**, 4603 (1987).
[5] N. S. Wang, E. R. Lovejoy, and C. J. Howard, J. Phys. Chem. **91**, 5743 (1987).
[6] CODATA, Supplement II, 1984 (see References in Introduction).
[7] NASA Evaluation No. 7, 1985 (see References in Introduction).
[8] NASA Evaluation No. 8, 1987 (see References in Introduction).

$HS + O_3 \rightarrow HSO + O_2$

$\Delta H^\circ = -287$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.2\pm1.0)\times10^{-12}$	298	Friedl, Brune, and Anderson, 1985[1]	(a)
$(3.9\pm0.8)\times10^{-12}$	298	Schoenle, Rahman, and Schindler, 1987[2]	(b)
Reviews and Evaluations			
3.2×10^{-12}	298	NASA, 1985[3]	(c)
9.7×10^{-12}	200–300	NASA, 1987[4]	(d)

Comments

(a) Discharge–flow study, He carrier gas. HS generated by $H + H_2S$ reaction. [HS] monitored by laser-induced fluorescence.

(b) Discharge–flow study, He carrier gas. HS produced by $F + H_2S$ reaction. [HS] and [HSO] monitored by mass spectrometry.

(c) Accepts value of Friedl *et al.*[1]

(d) Temperature coefficient taken from Wang and Howard.[5] Preexponential factor based on work of Wang and Howard,[5] Schoenle *et al.*[2], and Friedl *et al.*[1]

Preferred Values

$k = 3.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The two available measurements of k are in excellent agreement. The measurements of rate coefficients for other reactions of HS have shown that there are often unexpected sources of error in such work and for this reason we assign rather large error limits than the concordancy might warrant. We are also aware of a further unpublished confirmatory study of Wang and Howard[5] in which a small ($E/R = -20$ K) temperature coefficient is reported.

References

[1] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).

[2] G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **91**, 66 (1987).

[3] NASA Evaluation No. 7, 1985 (see References in Introduction).

[4] NASA Evaluation No. 8, 1987 (see References in Introduction).

[5] W. S. Wang and C. J. Howard (to be published).

$HS + NO + M \rightarrow HSNO + M$

$\Delta H^\circ \approx 140$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.4 \times 10^{-31}[N_2]$	298	Black, 1984[1]	(a)
$2.7 \times 10^{-31}(T/300)^{-2.48}[N_2]$	250–445	Black *et al.*, 1984[2]	(a)
$1.4 \times 10^{-30}[N_2]$	298	Bulatov, Kozliner, and Sarkisov, 1985[3]	(b)
Reviews and Evaluations			
$2.4 \times 10^{-31}(T/300)^{-3}$[air]	200–300	NASA, 1987[4]	(c)

Comments

(a) Laser flash photolysis of H_2S at 193 nm with HS detection by LIF at 354.5 nm. Pressure dependence studied over the range 30–760 Torr. Relative rates $k_0(He):k_0(Ar):k_0(N_2) = 0.88:0.92:1$. Falloff curves represented with $F_c = 0.6$ and $k_\infty = 2.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Theoretical modeling with the given ΔH°.

(b) Flash photolysis with intracavity laser spectroscopy of HSO. Measurements at 13 Torr.

(c) Based on Refs. 1 and 2.

Preferred Values

$k_0 = 2.4 \times 10^{-31}(T/300)^{-2.5}[N_2]$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Values

The pressure- and temperature-dependent measurements from Refs. 1 and 2 show a consistent picture for the association reaction and are preferred. The higher rate coefficients from Ref. 3 and earlier references, cited in Ref. 5 and attributed to an unspecified reaction HS + NO → products, have all been obtained in low pressure experiments. They may either have been influenced[1,2] by heterogeneous processes or by other reaction channels.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.8 \pm 1) \times 10^{-11}$	298	Black, 1984[1]	(a)
$(2.7 \pm 0.5) \times 10^{-11}$	250–300	Black *et al.*, 1984[2]	(a)
Reviews and Evaluations			
2.7×10^{-11}	200–300	NASA, 1987[4]	(b)

Comments

(a) See comment (a) for k_0.

(b) Based on Refs. 1 and 2.

Preferred Values

$k_\infty = 2.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

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

Comments on Preferred Values

The falloff extrapolation with $F_c = 0.6$ of Refs. 1 and 2 toward k_∞ appears less certain than that to k_0.

Intermediate Falloff Range

The given k_0 and k_∞ values from Refs. 1 and 2 were based on an assumed F_c-value of 0.6.

References

[1] G. Black, J. Chem. Phys. **80**, 1103 (1984).

[2] G. Black, R. Patrick, L. E. Jusinski, and T. G. Slanger, J. Chem. Phys. **80**, 4065 (1984).

[3] V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz. **4**, 1353 (1985).

[4] NASA Evaluation No. 8, 1987 (see References in Introduction).

[5] CODATA Supplement II, 1984 (see References in Introduction).

$HS + NO_2 \rightarrow HSO + NO$

$\Delta H^\circ = -88$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.4)\times10^{-11}$	298	Black, 1984[1]	(a)
$(2.4 \pm 0.2)\times10^{-11}$	298	Bulatov, Kozliner, and Sarkisov, 1984[2]	(b)
$(3.0 \pm 0.8)\times10^{-11}$	298	Friedl, Brune, and Anderson, 1985[3]	(c)
$(12.0 \pm 2.0)\times10^{-11}$	298	Schoenle, Rahman, and Schindler, 1987[4]	(d)
$(4.8\times1.0)\times10^{-11}$	298	Stachnik and Molina, 1987[5]	(e)
$2.9\times10^{-11}\exp(237/T)$	221–415 K	Wang, Lovejoy, and Howard, 1987[6]	(f)
$(6.7 \pm 1.0)\times10^{-11}$	298		
Reviews and Evaluations			
3.2×10^{-11}	298	NASA, 1985[7]	(g)
$2.9\times10^{-11}\exp(240/T)$	200–300	NASA, 1987[8]	(h)

Comments

(a) Pulsed laser dissociation of H_2S at 193 nm. Decay of [HS] monitored by laser-induced fluorescence. He, Ar, N_2 used as buffer gases. k independent of He pressure over range 28.5–300 Torr. $k(H + NO_2 + He) < \sim 7\times10^{-31}$ cm^6 molecule^{-2} s^{-1}.

(b) Pulsed laser photolysis of H_2S/NO_2 mixtures. [HSO] monitored by intracavity laser absorption.

(c) Discharge–flow study, He carrier gas. HS generated by $H + H_2S$;H_2S in excess. [HS] monitored by laser-induced fluorescence.

(d) Discharge–flow study, He carrier gas. HS generated by $F + H_2S$ reaction. [HS] monitored by mass spectrometry. [HSO] also monitored in some experiments.

(e) Pulsed laser photolysis of H_2S at 193 nm. [HS] monitored by absorption at 324 nm using multipass cell. O_2 added to suppress secondary chemistry arising from presence of H atoms. N_2 used as buffer gas; total pressures cover range 30–730 Torr.

(f) Discharge–flow study, He carrier gas. HS generated by $F + H_2S$ and $H + C_2H_4S$. [HS] monitored by laser magnetic resonance.

(g) Takes mean of results of Black[1] and Friedl *et al.*[3]

(h) Accepts value of Wang *et al.*[6]

Preferred Values

$k = 5.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.6\times10^{-11}\exp(240/T)$ cm^3 molecule^{-1} s^{-1} over range 220–450 K.

Reliability

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

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

Comments on Preferred Values

There is considerable scatter on the measured values of k with no obvious correlation with the conditions used or the technique. The presence of H atoms in the system is known to lead to complicating secondary chemistry, and some of the differences may be due to this, particularly where HS has been generated by photolysis of H_2S. In more recent studies[5,6] care has been taken to eliminate a model such effects, but significant differences persist. The preferred value at 298 K is the mean of the results of Stachnik and Molina[5] and Wang *et al.*[6] The temperature coefficient is that of Wang *et al.*[6]

References

[1]G. Black, J. Chem. Phys. **80**, 1103 (1984).
[2]V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz. **3**, 1300 (1984).
[3]R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).
[4]G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **91**, 66 (1987).
[5]R. A. Stachnik and M. J. Molina **91**, 4603 (1987).
[6]N. S. Wang, E. R. Lovejoy, and C. J. Howard, J. Phys. Chem. **91**, 5743(1987).
[7]NASA Evaluation No. 7, 1985 (see References in Introduction).
[8]NASA Evaluation No. 8, 1987 (see References in Introduction).

$HSO + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leqslant 2.0 \times 10^{-17}$	296	Lovejoy, Wang, and Howard, 1987[1]	(a)
Reviews and Evaluations			
$\leqslant 2.0 \times 10^{-17}$	298	NASA, 1987[2]	(b)

Comments

(a) Discharge–flow study. He carrier gas. HSO generated by $O + CH_3SH$ reaction. [HSO] monitored by laser magnetic resonance. No HO_2 or OH, which are possible reaction products, were observed.

(b) Value of Lovejoy *et al.*[1]

Preferred Values

$k \leqslant 2.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The reaction is slow and only an upper limit to k is available.

References

[1]E. R. Lovejoy, W. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).
[2]NASA Evaluation No. 8, 1987 (See References in Introduction).

$HSO + O_3 \rightarrow HS + 2O_2$ (1)
$\rightarrow HO + SO + O_2$ (2)

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

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
1.1×10^{-13}	298	Friedl, Brune, and Anderson, 1985[1]	(a)
Reviews and Evaluations			
1.0×10^{-13}	298	NASA, 1985[2]	(b)
1.0×10^{-13}	298	NASA, 1987[3]	(b)

Comments

(a) Discharge–flow system, He carrier gas. $HS + O_3$ reaction studied. HS generated by $H + H_2S$ reaction. [HS] monitored by laser-induced fluorescence. Addition of O_3 gives an initial fall in [HS], which finally goes to a steady state indicating regeneration of the HS, postulated to be by the $HSO + O_3$. Reaction $k/k(HS + O_3) = 0.031 \pm 0.005$ obtained. Using $k(HS + O_3) = 3.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (this volume) gives tabulated k. k also obtained by modeling [HS] profiles giving $k = (1.1 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for best fit.

(b) Accepts value of Friedl *et al.*[1]

Preferred Values

$k = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.8$ at 298 K.

Comments on Preferred Values

There is only one determination of this rate coefficient by an indirect method. We accept this value but assign wide error limits.

References

[1] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).

[2] NASA Evaluation No. 7, 1985 (see References in Introduction).

[3] NASA Evaluation No. 8, 1987 (see References in Introduction).

HSO + NO → products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.6×10^{-14}	298	Bulatov, Kozliner, and Sarkisov, 1985[1]	(a)
$\leqslant 1\times10^{-15}$	298	Lovejoy, Wang, and Howard, 1987[2]	(b)
Reviews and Evaluations			
1.0×10^{-15}	298	NASA, 1987[3]	(c)

Comments

(a) Pulsed laser photolysis of $H_2S/NO_2/NO$ mixtures. [HSO] monitored by intracavity laser absorption. Pressure varied from 10–100 Torr.

(b) Discharge–flow study, He carrier gas. HSO generated by O + CH_3SH and HS + NO_2 reactions. [HSO] monitored by laser magnetic resonance.

(c) Accepts result of Lovejoy *et al.*[1]

Preferred Values

$k \leqslant 1.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The only two available measurements of k differ by at least a factor of 26. This is unlikely to be due to the higher pressures used in the Bulatov *et al.*[1] study but may arise from secondary chemistry in their HSO source, which employed relatively large H_2S concentrations. Provisionally, the upper limit of Lovejoy *et al.*[2] is preferred.

References

[1] V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khimi. Fiz. **4**, 1353 (1985).

[2] E. R. Lovejoy, W. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).

[3] NASA Evaluation No. 8, 1987 (see References in Introduction).

HSO + NO_2 → products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
4.1×10^{-12}	298	Bulatov, Kozliner, and Sarkisov, 1984[1]	(a)
$(9.6\pm2.4)\times10^{-12}$	298	Lovejoy, Wang, and Howard, 1987[2]	(b)
Reviews and Evaluations			
9.8×10^{-12}	298	NASA, 1987[3]	(c)

Comments

(a) Pulsed laser photolysis of H_2S/NO_2 mixtures. [HSO] monitored by intracavity laser absorption.

(b) Discharge–flow study, He carrier gas. HSO generated by O + CH_3SH or HS + NO_2 reactions. [HSO], [HS], [HO], and [HO_2] monitored by laser magnetic resonance.

(c) Based on Lovejoy *et al.*[2]

Preferred Values

$k = 9.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The only two measurements of k differ by at least a factor of 2. Lovejoy *et al.*[2] have suggested that the relatively high H_2S concentrations used by Bulatov *et al.*[1] may lead to side reactions regenerating HSO. The value of Lovejoy *et al.*[2] is preferred, but wide error limits are assigned awaiting confirmatory studies.

HO_2 was observed as a product of the reaction by Lovejoy *et al.*, which they suggest arises from the sequence $HSO + NO_2 \rightarrow HSO_2 + NO$, $HSO_2 + O_2 \rightarrow HO_2 + SO_2$.

References

[1] V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khimi. Fiz. **3**, 988 (1984).

[2] E. R. Lovejoy, W. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).

[3] NASA Evaluation No. 8, 1987 (see References in Introduction).

$HSO_2 + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
3×10^{-13}	296	Lovejoy, Wang, and Howard, 1987[1]	(a)
Reviews and Evaluations			
3.0×10^{-13}	298	NASA, 1987[2]	(b)

Comments

(a) Discharge–flow study, He carrier gas. HSO generated by $O + CH_3SH$ and $HS + NO_2$ reactions. $HSO + NO_2$ reaction studied. [HSO], [HO_2], and [HO] monitored by laser magnetic resonance. O_2 addition to system leads to growth of [HO_2] assumed to be due to $HSO + NO_2 \rightarrow HSO_2 + NO$, $HSO_2 + O_2 \rightarrow HO_2 + SO_2$. k deduced from [HO_2] profile.

(b) Value of Lovejoy *et al.*[1]

Preferred Values

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

Reliability

$\Delta \log k = \pm 0.8$ at 298 K.

Comments on Preferred Values

The indirect nature of the sole measurement of k leads us to suggest substantial error limits despite the quality of the experimental work.

References

[1] E. R. Lovejoy, W. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).

[2] NASA Evaluation No. 8, 1987 (see References in Introduction).

$SO + NO_2 \rightarrow SO_2 + NO$

$\Delta H^\circ = -160$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.37 \pm 0.07) \times 10^{-11}$	210–363	Brunning and Stief, 1986[1]	(a)
$(1.37 \pm 0.07) \times 10^{-11}$	298		
Reviews and Evaluations			
1.4×10^{-11}	298	CODATA, 1984[2]	(b)
1.4×10^{-11}	298	NASA, 1985[3]	(c)
1.4×10^{-11}	200–300	NASA, 1987[4]	(d)

Comments

(a) Discharge–flow study, He carrier gas. SO generated by discharge in He/SO_2 mixture. [SO] determined by titration with NO_2. [SO] monitored by quadrapole mass spectrometry. Pseudo-first-order conditions

(b) Based on work of Black *et al.*,[5] Clyne *et al.*[6,7]

(c) Based on work cited in (b) and that of Brunning *et al.*[1]

Preferred Values

$k = 1.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 210–360 K.

Reliability

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

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

Comments on Preferred Values

The recent measurements of Brunning and Stief are the first on the temperature dependence of k and indicate no measurable change in k over the range 210–363 K. This finding is the basis for our present recommendation for the temperature coefficient. The new results are in good agreement at 298 K with our previous recommendation.

References

[1] J. Brunning and L. J. Stief, J. Chem. Phys. **84**, 4371 (1986).
[2] CODATA Supplement II, 1984 (see References in Introduction).
[3] NASA Evaluation No. 7, 1985 (see References in Introduction).
[4] NASA Evaluation No. 8, 1987 (see References in Introduction).
[5] G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).
[6] M. A. A. Clyne, C. J. Halstead, and B. A. Thrush, Proc. Roy. Soc. London, Ser. A **295**, 355 (1966).
[7] M. A. A. Clyne and A. J. MacRobert, Int. J. Chem. Kinet. **12**, 79 (1980).

$O_3 + CH_3SCH_3 \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<8.3\times10^{-19}$	296	Martinez and Herron, 1978[1]	(a)

Comments

(a) Static system with mass spectrometric detection of O_3.

Preferred Values

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

Comments on Preferred Values

The preferred value is based upon the sole study of Martinez and Herron.[1]

References

[1] R. I. Martinez and J. T. Herron, Int. J. Chem. Kinet. **10**, 433 (1978).

4.6. Fluorine Species

$F + O_2 + M \rightarrow FO_2 + M$

$\Delta H^\circ = -52.8$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.3\pm0.4)\times10^{-33}(T/300)^{-1}[Ar]$	295–359	Pagsberg *et al.*, 1987[1]	(a)
Reviews and Evaluations			
$1.3\times10^{-32}(T/300)^{-1.4}[N_2]$	200–300	CODATA, 1984[2]	(b)
$1.6\times10^{-32}(T/300)^{-1.4}[air]$	200–300	NASA, 1987[3]	(b,c)

Comments

(a) Pulse radiolysis of $Ar/F_2/O_2$ mixtures. UV absorption of FO_2 radicals recorded at 220 nm. Determination of the rate coefficient and the equilibrium constant by varying the O_2 concentration. The derived ΔH° value of the reaction is given above.

(b) Mostly based on earlier measurements[4–6] with $M = He$ and a single determination of the N_2:He relative efficiency from Ref. 7.

(c) Temperature coefficient estimated theoretically in Ref. 8.

Preferred Values

$k_0 = 4.3\times10^{-33}(T/300)^{-1.4}[N_2]$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Values

The new determination[1] appears more direct and internally consistent than the earlier work.[7] It is, therefore, preferred assuming $k(\mathrm{Ar}):k(\mathrm{N_2}) \approx 1$. The calculated temperature coefficient[8] is in accord with the experimental observation from Ref. 1.

References

[1] P. Pagsberg, E. Ratajczak, A. Sillesen, and J. T. Jodkowski, Chem. Phys. Lett. **141**, 88 (1987).
[2] CODATA Supplement II, 1984 (see References in Introduction).
[3] NASA Evaluation No. 8, 1987 (see References in Introduction).
[4] N. F. Shamonina and A. G. Ktov, Kinetika i Kataliz **20**, 233 (1979).
[5] C. Zetzsch, in *Proceedings of the 1st European Symposium on Combustion* (Academic, London, 1973), p. 35.
[6] H. L. Chen, D. W. Trainor, R. E. Center, and W. I. Fyfe, J. Chem. Phys. **66**, 5513 (1977).
[7] V. S. Arutymov, L. S. Popov, and A. M. Chaikin, Kinetika i Kataliz **17**, 286 (1976).
[8] R. Patrick and D. M. Golden, Int. J. Chem. Kinet. **15**, 1189 (1983).

$FO_2 + M \rightarrow F + O_2 + M$

$\Delta H^\circ = +52.8\ \mathrm{kJ\ mol^{-1}}$

Low-pressure rate coefficients
Rate coefficient data

$k_0/\mathrm{s^{-1}}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.3\times10^{-9}\exp(-5800/T)[\mathrm{Ar}]$	295–359	Pagsberg *et al.*, 1987[1]	(a)

Comments

(a) Pulse radiolysis of $\mathrm{Ar/F_2/O_2}$ mixtures. UV absorption of FO_2 radicals recorded at 220 nm. Analysis of the approach to the equilibrium as a function of O_2 pressure. The measured value at 1 atm of Ar and 295 K is $k_0 = 4.53\times10^{2}\ \mathrm{s^{-1}}$.

Preferred Values

$k_0 = 6.3\times10^{-9}\exp(-5800/T)[\mathrm{N_2}]\ \mathrm{s^{-1}}$ over the range 200–400 K.

$k_0 = 2.2\times10^{-17}[\mathrm{N_2}]\ \mathrm{s^{-1}}$ at 298 K.

Reliability

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

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

Comments on Preferred Values

The given Arrhenius expression from this evaluation of Ref. 1 is based on the assumption that the rates for M = Ar and N_2 are equal. Earlier estimates[2,3] based on the reverse reaction and estimated heats of formation of FO_2 considerably differ from this first direct measurement of the equilibrium.

References

[1] P. Pagsberg, E. Ratajczak, A. Sillesen, and J. T. Jodkowski, Chem. Phys. Lett. **141**, 88 (1987).
[2] CODATA Supplement II, 1984 (see References in Introduction).
[3] NASA Evaluation No. 8, 12 987 (see References in Introduction).

$HO + CH_3CHF_2 \rightarrow H_2O + CH_2CHF_2$ (1)
$\rightarrow H_2O + CH_3CF_2$ (2)

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

$k/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.1\pm0.7)\times10^{-14}$	296	Howard and Evenson, 1976[1]	(a)
$(3.5\pm0.5)\times10^{-14}$	293	Handwerk and Zellner, 1978[2]	(b)
$(3.0^{+1.0}_{-0.8})\times10^{-12}\exp[-(1200\pm100)/T]$	293–417	Clyne and Holt, 1979[3]	(c)
$(4.66\pm0.16)\times10^{-14}$	293		
$(3.70\pm0.37)\times10^{-14}$	297	Nip *et al.*, 1979[4]	(b)
Reviews and Evaluations			
3.4×10^{-14}	295	Atkinson, 1986[5]	(d)
$1.9\times10^{-12}\exp(-1200/T)$	293–417	NASA, 1987[6]	(e)

Comments

(a) Discharge flow–laser magnetic resonance detection of HO.

(b) Flash photolysis-resonance absorption detection of HO.

(c) Discharge flow–resonance fluorescence detection of HO.

(d) Mean of the room-temperature rate coefficients of Howard and Evenson,[1] Handwerk and Zellner,[2] and Nip *et al.*[4] The data of Clyne and Holt[3] were not used in the evaluation.

(e) The room-temperature rate coefficient is the mean of the room-temperature rate coefficients of Howard and Evenson,[1] Handwerk and Zellner,[2] and Nip *et al.*[4] (as in the evaluation of Atkinson[5]). The temperature dependence is that determined by Clyne and Holt,[3] with the A factor being adjusted to fit the 298 K rate coefficient.

Preferred Values

$k = 3.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

As for the Atkinson[5] and NASA[6] evaluations, the room-temperature rate coefficient is the mean of those determined by Howard and Evenson,[1] Handwerk and Zellner,[2] and Nip *et al.*[4] Since the Clyne and Holt[3] data are not used in the evaluation of the 298 K rate coefficient, their temperature dependence data are not used and no temperature-dependent expression is recommended.

References

[1] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 4303 (1976).
[2] V. Handwerk and R. Zellner, Ber. Bunsenges. Phys. Chem. **82**, 1161 (1978).
[3] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2 **75**, 582 (1979).
[4] W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. **83**, 2440 (1979).
[5] R. Atkinson, Chem. Rev. **86**, 69 (1986).
[6] NASA Evaluation No. 8, 1987 (see References in Introduction).

$HO + CH_2FCF_3 \rightarrow H_2O + CHFCF_3$

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.2^{+2.3}_{-1.3}) \times 10^{-12} \exp[-(1800 \pm 200)/T]$	294–429	Clyne and Holt, 1979[1]	(a)
$(5.5 \pm 0.7) \times 10^{-15}$	294		
$(5.15 \pm 0.58) \times 10^{-15}$	298	Martin and Paraskevopoulos, 1983[2]	(b)
$1.22 \times 10^{-25} T^{(4.36 \pm 1.14)} \exp[+(45 \pm 388)/T]$	249–473	Jeong *et al.*, 1984[3]	(c)
$(8.44 \pm 0.73) \times 10^{-15}$	298		
Review and Evaluations			
$1.27 \times 10^{-18} T^2 \exp(-769/T)$	249–473	Atkinson, 1986[4]	(d)
$6.6 \times 10^{-13} \exp(-1300/T)$	249–473	NASA, 1987[5]	(e)

Comments

(a) Discharge flow–resonance fluorescence detection of HO.

(b) Flash photolysis–resonance absorption detection of HO.

(c) Rate coefficients also fit to an Arrhenius expression, yielding $k = (1.10 \pm 0.11) \times 10^{-12} \exp[-(1424 \pm 35)/T]$ cm^3 molecule^{-1} s^{-1}.

(d) Obtained from a least-squares analysis of the absolute rate coefficients of Martin and Paraskevopoulos[2] and Jeong *et al.*,[3] using the three-parameter expression $k = CT^2 e^{-D/T}$. The data of Clyne and Holt[1] were not utilized in the evaluation because of discrepancies with other data for the haloalkanes.[4]

(e) Obtained from a least-squares analysis of the absolute rate coefficients of Martin and Paraskevopoulos[2] and Jeong *et al.*[3]

Preferred Values

$k = 8.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.6 \times 10^{-13} \exp(-1300/T)$ cm^3 molecule^{-1} s^{-1} over the range 250–440 K.

Reliability

$\Delta \log k = \pm 0.2$.

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

Comments on Preferred Values

The preferred value is derived from a least-squares analysis of the rate coefficients of Martin and Paraskevopoulos[2] and Jeong *et al.*[3] to the three-parameter equation $k = CT^2 e^{-D/T}$, yielding $k = 1.27 \times 10^{-18} T^2 \exp(-769/T)$. The preferred Arrhenius expression, $k = A \exp(-B/T)$, which agrees with the NASA evaluation,[5] is centered at 265 K with $A = Ce^2T^2$ and $B = D + 2T$.

References

[1] M. A. A. Clyne and P. M. Holt, J. Chem. Soc., Faraday Trans. 2 **75**, 582 (1979).

[2] J.-P. Martin and G. Paraskevopoulos, Can. J. Chem. **61**, 861 (1983).

[3] K.-M. Jeong; K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. **88**, 1222 (1984).

[4] R. Atkinson, Chem. Rev. **86**, 69 (1986).

[5] NASA Evaluation No. 8, 1987 (See References in Introduction).

4.7. Chlorine Species

$O + HOCl \rightarrow HO + ClO$

$\Delta H^\circ = -30$ kJ mol^{-1}

Comments

There are still no experimental data on this reaction. In this evaluation we prefer to make no recommendation, rather than the estimated preferred value of $1 \times 10^{-11} \exp(-2200/T)$ given in our previous evaluation.[1]

References

[1] CODATA Supplement II, 1984 (see References in Introduction).

$O + ClO \rightarrow Cl + O_2$

$\Delta H^\circ = -230$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.5) \times 10^{-11}$	252–347	Schwab *et al.*, 1984[1]	(a)
$(1.55 \pm 0.33) \times 10^{-11} \exp[(263 \pm 60)/T]$	231–367	Nicovich, Wine, and Ravishankara, 1988[2]	(b)
$(3.8 \pm 0.6) \times 10^{-11}$	298		
Relative Rate Coefficients			
$(3.5 \pm 0.6) \times 10^{-11}$	298	Ongstad and Birks, 1984[3]	(c)
$(2.61 \pm 0.60) \times 10^{-11} \exp[(97 \pm 64)/T]$	220–387	Ongstad and Birks, 1986[4]	(c)
Reviews and Evaluations			
$6.4 \times 10^{-11} \exp(-120/T)$	220–370	CODATA[5]	(d)
$4.7 \times 10^{-11} \exp(-50/T)$	200–300	NASA, 1985[6]	(e)
$3.0 \times 10^{-11} \exp(70/T)$	200–300	NASA, 1987[7]	(f)

Comments

(a) Discharge flow–LMR detection of ClO; resonance fluorescence of O and Cl. Pseudo-first-order decay of O in presence of excess ClO and ClO in excess O gave good agreement in k. No discernible temperature dependence over range studied. Pressure range 0.8–2.0 Torr.

(b) Dual laser flash photolysis–resonance fluorescence in slow flow system. ClO produced by reaction of excess Cl, produced by 351 nm excimer laser photolysis of Cl_2, with a known amount of O_3. O produced by 266 nm laser photolysis of ClO after appropriate delay time. O monitored by time-resolved resonance fluorescence. Correction of overall O decay rate for loss due to reaction with Cl_2 and other routes. Pressure range of 25–500 Torr, $M = N_2$. No pressure effect on k.

(c) Discharge flow–detection of O by $NO + O + M$ chemiluminescence in presence of excess ClO. [ClO] determined indirectly by *in situ* conversion to NO_2 by addition of NO and k measured relative to $k(O + NO_2 \Rightarrow NO + O_2) = (6.58 \pm 0.52) \times 10^{-12} \exp[(142 \pm 23)/T]$ cm^3 molecule^{-1} s^{-1}, determined in the same system concurrently. Pressure = 2.3 Torr. No effect of O_2 at 230 K.

(d) Based on results of Leu,[8] Margitan,[9] and earlier studies of Bemand *et al.*,[10] Clyne and Nip,[11] and Zahniser and Kaufman.[12]

(e) Based on least-squares fit to data below 370 K from all studies except the most recent ones from Ongstad and Birks[4] and Nicovich *et al.*[2]

(f) Based on a least-squares fit to data from Leu,[8] Margitan,[9] Schwab *et al.*,[1] Ongstad and Birks,[3,4] Zahniser and Kaufman,[12] and Nicovich *et al.*[2]

Preferred Values

$k = 3.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

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

Comments on Preferred Values

The most recent studies all give values of $k_{298\ K}$ about 30% lower than the earlier work of Bemand *et al.*[10] and Clyne and Nip.[11] The two most recent studies[2,4] give a negative temperature dependence, in contrast to the earlier work, which showed zero or positive temperature coefficients. The preferred value is independent of temperature and is obtained by averaging the 298 K values from the six studies used as a basis for the NASA evaluation. The uncertainty on E/R allows for a temperature dependence consistent with all studies. Leu and Yung[13] have recently shown that the yields of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ in the reaction are $<2.5\times10^{-2}$ and $(4.4\pm1.1)\times10^{-4}$, respectively.

References

[1] J. J. Schwab, D. W. Toohey, W. H. Brune, and J. G. Anderson, J. Geophys. Res. **89**, 9581 (1984).

[2] J. M. Nicovich, P. H. Wine, and A. R. Ravishankara, J. Chem. Phys. **89**, 5670 (1988).

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

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

[5] CODATA Supplement II, 1984 (see References in Introduction).

[6] NASA Evaluation No. 7, 1985 (see References in Introduction).

[7] NASA Evaluation No. 8, 1987 (see References in Introduction).

[8] M. T. Leu, J. Phys. Chem. **88**, 1394 (1984).

[9] J. J. Margitan, J. Phys. Chem. **88**, 3638 (1984).

[10] P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday 1 **69**, 1356 (1973).

[11] M. A. A. Clyne and W. S. Nip, J. Chem. Soc. Faraday 1 **72**, 221 (1976).

[12] M. S. Zahniser and F. Kaufman, J. Chem. Phys. **66**, 3673 (1977).

[13] M. T. Leu and Y. Yung, Geophys. Res. Lett. **14**, 949 (1987).

$O + OClO \rightarrow O_2 + ClO$ (1)
$\rightarrow O + ClOO$ (2)

$\Delta H^\circ(1) = 248\ \text{kJ mol}^{-1}$
$\Delta H^\circ(2) = -7\ \text{kJ mol}^{-1}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5^{+1}_{-2})\times10^{-13}$	298	Bemand, Clyne, and Watson, 1973[1]	(a)
Reviews and Evaluations			
5.0×10^{-13}	298	Watson, 1977[2]	(b)
$2.8\times10^{-11}\exp(-1200/T)$	200–300	NASA, 1987[3]	(c)

Comments

(a) Discharge flow–resonance fluorescence detection of $O(^3P)$ and mass spectrometric detection of OClO. k determined from $O(^3P)$ decay in excess OClO and OClO decay in excess $O(^3P)$ with NOCl added to prevent secondary reactions, which lead to enhanced OClO decay, attributed to reaction of Cl with OClO. Only fair agreement between two methods, the $O(^3P)$ decay method giving somewhat higher values.

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

(c) Arrhenius expression was estimated on the basis of the 298 K data of Bemand *et al.*[1]

Preferred Values

$k = 5\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is based on the data of Bemand *et al.*[1] Earlier estimates of k from flash photolysis work[4,5] giving much higher values for this rate coefficient were shown to be due to autocatalysis involving the reactions $O + ClO \rightarrow Cl + O_2$ and $Cl + OClO \rightarrow 2ClO$. The possibility of the occurrence of the second exothermic channel does not appear to have been considered. This channel could also lead to autocatalysis, since ClOO dissociates rapidly to $Cl + O_2$. The results obtained with ClNO scavenger in Ref. 1 show, however, that channel (2) cannot be much greater than the normally assumed reaction pathway.

References

[1] P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday 1 **69**, 1356 (1973).

[2] R. T. Watson, J. Phys. Chem. Ref. Data **6**, 871 (1977).

[3] NASA Evaluation No. 8, 1987 (see References in Introduction).

[4] F. J. Lipscomb, R. G. W. Norrish, and B. A. Thrush, Proc. Roy. Soc. **A233**, 455 (1956).

[5] N. Basco and S. K. Dogra, Proc. Roy. Soc. London Ser. A **323**, 29 (1971).

$Cl + HO_2 \rightarrow HCl + O_2$ (1)
$\rightarrow ClO + HO$ (2)

$\Delta H^\circ(1) = -228.2$ kJ mol^{-1}
$\Delta H^\circ(2) = 5$ kJ mol^{-1}

Comments

Cattell and Cox,[1] using a molecular modulation technique over the pressure range 50–760 Torr, report results for both the overall rate constant and the relative contribution of the two channels in good agreement with those of Lee and Howard,[2] upon which the previous evaluation[3] was based. Neither channel shows any pressure dependence between 1 and 760 Torr, showing that stabilization of the HOOCl* intermediate does not occur, the two bimolecular channels making up the entire reaction pathway. There is no change in the preferred values for k_1 and k_2.

References

[1] F. C. Cattell and R. A. Cox, J. Chem. Soc. Faraday Trans. 2 **82**, 1413 (1986).
[2] Y.-P. Lee and C. J. Howard, J. Chem. Phys. **77**, 756 (1982).
[3] CODATA Supplement II, 1984 (see References in Introduction).

$Cl + O_2 + M \rightarrow ClOO + M$

$\Delta H^\circ = -27$ kJ mol^{-1}

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.6\times10^{-34}[Ar]$	200–300	Clyne and Coxon, 1968[1]	(a)
$1.7\times10^{-33}[N_2+O_2]$	300	Nicholas and Norrish, 1968[2]	(b)
Reviews and Evaluations			
$2.0\times10^{-33}(T/300)^{-1.4}[N_2]$	200–300	NASA, 1987[3]	(c)

Comments

(a) Measurements attributed to D. H. Stedman. Discharge flow–Cl monitored by chlorine afterglow emission.

(b) Flash photolysis of Cl_2–O_2 mixtures. k determined by complex analysis of the time-resolved production of ClO measured by photographic recording of absorption in the UV region.

(c) Based on data in Refs. 1 and 2. The bath gas in Ref. 2 is erroneously referred to in Ref. 3 as Ar when in fact $N_2 + O_2$ was used.

Preferred Values

$k = 1.7\times10^{-33}[N_2]$ 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 for this reaction are very sparse considering its potential significance. The study of Nicholas and Norrish[2] was limited both in accuracy and precision due to the measurement technique and limited amount of data. The work of Stedman is only briefly referred to in Ref. 1. The preferred value is based on the data of Nicholas and Norrish for $M = N_2 + O_2$. No temperature dependence is recommended in the absence of experimental data at other temperatures.

References

[1] M. A. A. Clyne and J. A. Coxon, Proc. Roy. Soc. London Ser. A **303**, 207 (1968).
[2] J. E. Nicholas and R. G. W. Norrish, Proc. Roy. Soc. London Ser. A **307**, 391 (1968).
[3] NASA Evaluation No. 8, 1987 (see References in Introduction).

$ClOO + M \rightarrow Cl + O_2 + M$

$\Delta H^\circ = 27$ kJ mol^{-1}

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.67\times10^{-13}[N_2]$	298	Johnston, Morris, and Van den Bogaerde, 1969[1]	(a) (b)
$2.55\times10^{-13}[N_2]$	298	Ashford, Basco, and Hunt, 1978[2]	(a) (c)
$3.15\times10^{-13}[N_2]$	298	Cox *et al.*, 1979[3]	(a) (d)

Comments

(a) Value of k calculated from the equilibrium constant $K(Cl + O_2 \rightleftarrows ClOO)$, together with the reverse reaction for which $k = 1.7\times10^{-33}[N_2]$ cm^3 molecule^{-1} s^{-1} (this evaluation) assumed independent of temperature.

(b) $K = 3.64\times10^{-21}$ cm^3 molecule^{-1} from analysis of complex systems. Molecular modulation–UV spectroscopy to monitor ClOO and ClO kinetics in $Cl_2 + O_2$ photolysis at room temperature.

(c) Flash photolysis of $Cl_2 + O_2$–UV spectroscopic measurements of ClOO and ClO kinetics. $K = 6.64\times10^{-21}$ cm^3 molecule^{-1} at 298 K ($\pm$ factor of 2) from analysis of complex system.

(d) Molecular modulation–UV absorption detection of ClOO and ClO. Similar study to Ref. 1, but used more up-to-date thermodynamic and kinetic data to extract K. Use of the ΔH° gives $k_0 = 4.58\times10^{-6}\,T^{-1}\exp(-3217/T)[N_2]$ s^{-1}.

Preferred Values

$k = 2.4\times10^{-13}[N_2]$ s^{-1} at 298 K.

$k = 1.5\times10^{-8}\exp(-3285/T)[N_2]$ s^{-1} over range 200–300 K.

Reliability

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

$\Delta (E/R) = \pm 1250$ K.

Comments on Preferred Values

All three studies give excellent agreement in the quantity $K(k_1 + k_2)$, where k_1 and k_2 are the 298 K rate coefficients for the reactions: $Cl + ClOO \rightarrow Cl_2 + O_2$(1) and $Cl + ClOO \rightarrow ClO + ClO$(2). There is less good agreement in the values of k_1 and k_2, the value of σ_{ClOO} and other derived kinetic parameters in the systems. The results of Ashford *et al.*[2] and Cox *et al.*[3] seem more consistent with the body of information on the reactions of ClOO and ClO. The average of these data for K are used together with $k(Cl + O_2 + M)$ from this evaluation to obtain k_{298}. The temperature dependence assumes $k(Cl + O_2 + M)$ is temperature independent, with an activation energy equal to the reaction enthalpy.

References

[1] H. S. Johnston, E. D. Morris, and J. Van den Bogaerde, J. Amer. Chem. Soc. **91**, 7712 (1969).

[2] R. D. Ashford, N. Basco, and J. E. Hunt, Int. J. Chem. Kinet. **10**, 1233 (1978).

[3] R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and H. J. Reid, J. Chem. Soc. Faraday Trans. I **75**, 1648 (1979).

$Cl + O_3 \rightarrow ClO + O_2$

$\Delta H^\circ = -162$ kJ mol^{-1}

Comments

The recent work of Choo and Leu,[1] using discharge flow–chemiluminescence detection of $O_2(^1\Sigma)$ and $O_2(^1\Delta)$, showed that the yields of these two excited states of O_2 in the $Cl + O_3$ reaction was $<5\times10^{-4}$ and $<2.5\times10^{-2}$, respectively. This refutes the suggestion of Vanderzanden and Birks[2] that the production of oxygen atoms in the $Cl + O_3$ system was due to formation of 0.1%–0.5% $O_2(^1\Sigma)$ in this reaction.

References

[1] K. Y. Choo and M. T. Leu, J. Phys. Chem. **89**, 4832 (1985).

[2] J. W. Vanderzanden and J. W. Birks, Chem. Phys. Lett. **88**, 109 (1982).

$Cl + HNO_3 \rightarrow HCl + NO_3$

$\Delta H^\circ = -5.7$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<5.0\times10^{-16}$	298	Zagogianni, Mellouki, and Poulet, 1987[1]	(a)
$<2.0\times10^{-16}$	298–400	Wine, Wells, and Nicovich, 1988[2]	(b)
Reviews and Evaluations			
$<1.7\times10^{-14}$	298	CODATA, 1984[3]	(c)
$<1.7\times10^{-14}$	298	NASA, 1987[4]	(c)

Comments

(a) Discharge flow–EPR detection of Cl in excess HNO_3. The same upper limit was found for the reaction of ClO with HNO_3.

(b) Laser photolysis of Cl_2–HNO_3 mixtures at 351 nm. Reaction followed by observation of NO_3 formation using long path laser absorption spectroscopy, and also by monitoring Cl atom decay by resonance fluorescence. No evidence found for any reaction between Cl and HNO_3.

(c) Based on the work of Kurylo *et al.*[5]

Preferred Value

$k < 2.0\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

The new data show that the measurements of Kurylo *et al.*,[5] upon which previous recommended upper limits were based, are well above the true value for the rate coefficient of this reaction. The value of (E/R) reported by Kurylo *et al.* must also be incorrectly assigned to this reaction. The preferred upper limit is based on the work of Wine *et al.*[2]

References

[1] H. Zagogianni, A. Mellouki, and G. Poulet, Comp. Rendus Acad. Sci., Series **2**, 573 (1987).

[2] P. H. Wine, J. R. Wells, and J. M. Nicovich, J. Phys. Chem. **92**, 2223 (1988).

[3] CODATA Supplement II, 1984 (see References in Introduction).

[4] NASA Evaluation No. 8, 1987 (see References in Introduction).

[5] M. J. Kurylo, J. L. Murphy, and G. L. Knable, Chem. Phys. Lett. **94**, 281 (1983).

$Cl + NO_3 \rightarrow ClO + NO_2$

$\Delta H^\circ = -58.9$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.6\pm0.5)\times10^{-11}$	298	Mellouki, Le Bras, and Poulet, 1987[1]	(a)
Relative Rate Coefficients			
$(7.6\pm1.1)\times10^{-11}$	296	Cox *et al.*, 1984[2]	(b)
$(2.7\pm1.0)\times10^{-11}$	298	Burrows, Tyndall, and Moortgat, 1985[3]	(c)
$(5.5\pm2.0)\times10^{-11}$	278–338	Cox *et al.*, 1987[4]	(d)
Reviews and Evaluations			
5.2×10^{-11}	200–300	NASA, 1987[5]	(e)

Comments

(a) Discharge flow–EPR detection of Cl and NO, which was used to titrate NO_3. Pseudo-first-order decay of Cl in excess NO_3. Pressure = 0.8 Torr.

(b) Time dependent measurements of NO_3 absorption at 662 nm in the photolysis of Cl_1–$ClONO_2$–N_2 mixtures. First-order loss of NO_3 assumed to be due to reaction with Cl and k determined from steady-state [Cl] computed from model chemistry. k relative to $k(Cl + ClONO_2) = 1.18\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. $\sigma_{NO_3} = 1.7\times10^{-17}$ cm^2 molecule^{-1} at 662 nm. Pressure = 1 atm.

(c) $[NO_3]_{ss}$ measured by absorption in steady-state photolysis of Cl_2–$ClONO_2$–N_2 mixtures. k relative to $k(Cl + ClONO_2) = 1.18\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. Used $\sigma_{NO_3} = 1.85\times10^{-17}$ cm^2 molecule^{-1} at 662 nm.

(d) $[NO_3]_{ss}$ measured in modulated photolysis of Cl_2–$ClONO_2$–N_2 mixtures. k relative to $k(Cl + ClONO_2) = 1.18\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. $\sigma_{NO_3} = 1.7\times10^{-17}$ cm^2 molecule^{-1} at 662 nm. Pressure = 1 atm.

(e) Averaged of values from Cox *et al.*[2,4] and Burrows *et al.*[3]

Preferred Value

$k = 2.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Value

The agreement between the earlier relative rate measurements is not good and probably arises from complication in the chemistry of the systems used. The preferred value is based on the recent direct measurement from Mellouki *et al.*[1]

References

[1] A. Mellouki, G. Le Bras, and G. Poulet, J. Phys. Chem. **91**, 5760 (1987).

[2] R. A. Cox, R. A. Barton, E. Ljundstrom, and D. W. Stocker, Chem. Phys. Lett. **108**, 228 (1984).

[3] J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, J. Phys. Chem. **89**, 4848 (1985).

[4] R. A. Cox, M. Fowles, D. Moulton, and R. P. Wayne, J. Phys. Chem. **91**, 3361 (1987).

[5] NASA Evaluation No. 8, 1987 (see References in Introduction).

$Cl + C_3H_8 \rightarrow HCl + n\text{-}C_3H_7$ (1)
$\rightarrow HCl + i\text{-}C_3H_7$ (2)

$\Delta H^\circ(1) = -13.7$ kJ mol^{-1}
$\Delta H^\circ(2) = -29.5$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.36\pm0.13)\times10^{-10}\exp[(44\pm25)/T]$	220–607	Lewis *et al.*, 1980[1]	(a)
$(1.51\pm0.06)\times10^{-10}$	298		
Relative Rate Coefficiencts			
$6.6\times10^{-11}\exp(250/T)$	298–484	Pritchard, Pyke, and Trotman-Dickenson, 1955[2]	(b)
1.53×10^{-10}			
$k_1 = 3.3\times10^{-11}\exp(245/T)$	298	Knox and Nelson, 1959[3]	(c)
$k_2 = 4.7\times10^{-11}\exp(84/T)$	~200–500		
1.37×10^{-10}	298		
1.20×10^{-10}	296	Atkinson and Aschmann, 1985[4]	(d)
Reviews and Evaluations			
$1.4\times10^{-10}\exp(40/T)$	220–607	NASA, 1985[5]	(e)
$1.4\times10^{-10}\exp(40/T)$	220–607	NASA, 1987[6]	(e)

Comments

(a) Discharge flow–resonance fluorescence detection of Cl.

(b) Relative rate method. Cl atoms generated by photolysis of Cl_2. Relative disappearance rates of CH_4 and C_2H_6 and of C_2H_6 and C_3H_8 measured. The rate coefficient ratios $k(Cl + C_2H_6)/k(Cl + CH_4) = 4.67 \exp(1434/T)$ and $k(Cl + C_3H_8)/k(Cl + C_2H_6) = 1.47 \exp(166/T)$ were measured, leading to $k(Cl + C_3H_8)/k(Cl + CH_4) = 6.86 \exp(1600/T)$. Placed on an absolute basis using $k(Cl + CH_4) = 9.6\times10^{-12} \exp(-1350/T)$ cm^3 molecule^{-1} s^{-1}.[5-7]

(c) Relative rate method. Cl atoms generated by photolysis of Cl_2. Relative rate coefficients determined from the formation rates of alkyl chloride products. The rate constant ratios $k_1/k(Cl + C_2H_6) = 0.78 \exp(181/T)$ and $k_2/k(Cl + C_2H_6) = 1.11 \exp(20/T)$ were determined. With the relative rate coefficient $k(Cl + C_2H_6)/k(Cl + CH_4) = 4.4 \exp(1414/T)$,[8,9] this results in $k(Cl + C_3H_8)/k(Cl + CH_4) = [4.88 \exp(1434/T) + 3.43 \exp(1595/T)]$. Placed on an absolute basis by use of $k(Cl + CH_4) = 9.6\times10^{-12} \exp(-1350/T)$ cm^3 molecule^{-1} s^{-1}.[5-7]

(d) Relative rate method. Cl atoms generated by photolysis of Cl_2 in 1 atm of air. Relative disappearance rates of the organics studied were measured, leading to $k(Cl + C_3H_8)/k(Cl + n\text{-}C_4H_{10}) = 0.681$ and $k(Cl + C_2H_6)/k(Cl + n\text{-}C_4H_{10}) = 0.324$. This results in $k(Cl + C_3H_8)/k(Cl + C_2H_6) = 2.10$. Placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1}.[5-7]

(e) Based on the absolute rate coefficient data of Lewis *et al.*[1]

Preferred Values

$k = 1.5\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3\times10^{-10} \exp(40/T)$ cm^3 molecule^{-1} s^{-1} over the range 220–600 K.

Reliability

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

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

Comments on Preferred Values

The preferred rate coefficient is based upon the absolute rate coefficient data of Lewis *et al.*,[1] which are in generally good agreement with the relative rate measurements of Pritchard *et al.*,[2] Knox and Nelson,[3] and Atkinson and Aschmann.[4]

References

[1] R. S. Lewis, S. P. Sander, S. Wagner, and R. J. Watson, J. Phys. Chem. **84**, 2009 (1980).

[2] H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, J. Am. Chem. Soc. **77**, 2629 (1955).

[3] J. H. Knox and R. L. Nelson, Trans. Faraday Soc. **55**, 937 (1959).

[4] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

[5] NASA Evaluation No. 7, 1985 (see References in Introduction).

[6] NASA Evaluation No. 8, 1987 (see References in Introduction).

[7] CODATA, Supplement II, 1984 (see References in Introduction).

[8] J. H. Knox, Chem. Ind. **1955**, 1631.

[9] C. L. Lin, M. T. Leu, and W. B. DeMore, J. Phys. Chem. **82**, 1772 (1978).

$Cl + CH_3CHO \rightarrow HCl + CH_3CO$ (1)
$\rightarrow HCl + CH_2CHO$ (2)

$\Delta H^\circ(1) = -72.1$ kJ mol^{-1}

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

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
7.6×10^{-11}	298	Niki *et al.*, 1985[1]	(a)
Branching Ratio			
$k_2/k < 0.01$	298	Niki *et al.*, 1985[1]	(a)

Comments

(a) Cl atoms generated by photolysis of Cl_2 at >300 nm at 700 Torr total pressure of N_2. Rate coefficients k determined relative to that for the reaction of Cl atoms with C_2H_6, with $k(Cl + CH_3CHO)/k(Cl + C_2H_6) = 1.34 \pm 0.04$. Placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.7 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[2–4] The branching ratio of $k_2/k < 0.01$ was determined from an FT-IR spectroscopic product analysis.

Preferred Values

$k = 7.6 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$k_2/k < 0.01$ at 298 K.

Reliability

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

Comments on Preferred Values

The preferred values are those of Niki *et al.*,[1] with expanded uncertainty limits.

References

[1] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **89**, 588 (1985).

[2] CODATA, Supplement II, 1984 (see References in Introduction).

[3] NASA Evaluation No. 7, 1985 (see References in Introduction).

[4] NASA Evaluation No. 8, 1987 (see References in Introduction).

$Cl + CH_3CN \rightarrow$ products

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leqslant 2.0 \times 10^{-15}$	298	Kurylo and Knable, 1984[1]	(a)
$(3.46 \pm 0.70) \times 10^{-11} \exp[-(2785 \pm 115)/T]$	478–723	Poulet *et al.*, 1984[2]	(b)
$(8.89 + 1.24) \times 10^{-15}$	295		
Relative Rate Coefficients			
$8 \times 10^{-11} \exp(-3000/T)$	370–413	Olbregts, Brasseur, and Arijs, 1984[3]	(c)
Reviews and Evaluations			
$< 2.0 \times 10^{-15}$	298	NASA, 1985[4]	(d)
$< 2.0 \times 10^{-15}$	298	NASA, 1987[5]	(d)

Comments

(a) Flash photolysis–resonance fluorescence detection of Cl.

(b) Discharge flow–mass spectrometer detection of Cl. Data obtained over the range 295–723 K, and a curved Arrhenius plot was observed.

(c) Relative rate method. Relative formation rates of products monitored in a competitive chlorination system between CH_3CN and $CHCl_3$. Placed on an absolute basis by use of $k(Cl + CHCl_3) = 1.15 \times 10^{-11} \exp(-1686/T)$ cm^3 $molecule^{-1}$ s^{-1}.

(d) Based upon the upper limit to the rate coefficient measured by Kurylo and Knable.[1]

Preferred Value

$k \leqslant 2 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Comments on Preferred Value

Accepts the NASA[4,5] recommendations. The low-temperature ($\leqslant$410 K) rate coefficient data of Poulet *et al.*[2] could have been influenced by a heterogeneous reaction. The rate coefficients of Olbregts *et al.*[3] at 370 and 413 K are in good agreement with the higher-temperature data of Poulet *et al.*[2]

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] J. Olbregts, G. Brasseur, and E. Arijs, J. Photochem. **24**, 315 (1984).
[4] NASA Evaluation No. 7, 1985 (See References in Introduction).
[5] NASA Evaluation No. 8, 1987 (see References in Introduction).

$Cl + OClO \rightarrow ClO + ClO$

$\Delta H^\circ = -18$ kJ mol^{-1}

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$> 1.0 \times 10^{-12}$	300	Clyne and Coxon, 1968[1]	(a)
$(8.5 \pm 1.2) \times 10^{-12}$	300	Basco and Dogra, 1971[2]	(b)
$(5.9 \pm 0.9) \times 10^{-11} \exp[-(0 \pm 120)/T]$	298–588	Bemand, Clyne, and Watson, 1973[3]	(c)
$(5.9 \pm 0.9) \times 10^{-11}$	298		
$(6.1 \pm 0.9) \times 10^{-11}$	298		
$3.1 \times 10^{-11} \exp(160/T)$	228–450	Toohey, Brune, and Anderson, 1988[4]	(d)
5.45×10^{-11}	298		
Relative Rate Coefficients			
$(3.7 \pm 0.3) \times 10^{-10} \exp[-(3020 \pm 101)/T]$	335–365	Gritsan, Panfilov, and Sukhanov, 1975[5]	(e)
Reviews and Evaluations			
5.9×10^{-11}	298–588	Watson, 1977[6]	(f)
5.9×10^{-11}	200–300	NASA, 1985[7]	(f)
5.9×10^{-11}	200–300	NASA, 1987[8]	(f)

Comments

(a) Discharge flow–UV absorption of OClO and ClO product. Lower limit only determined.

(b) Flash photolysis of OClO–UV absorption detection of OClO and ClO.

(c) Discharge flow–resonance fluorescence detection of Cl decay in excess OClO and mass spectrometric determination of OClO decay in excess Cl. The first 298 K value is the average obtained from the two techniques; temperature independence is determined from Cl atom decay data at 300, 431, and 588 K. The second 298 K value was obtained from OClO decay in the presence of excess NO and Cl, in the unscavenged NO + OClO reaction at large extents of reaction.

(d) Discharge flow–resonance fluorescence detection of Cl.

(e) Thermal decomposition of OClO. Complex system.

(f) Based on data of Bemand *et al.*[3]

Preferred Values

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

$k = 3.4 \times 10^{-11} \exp(160/T)$ cm^3 $molecule^{-1}$ s^{-1} over range 298–450 K.

Reliability

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

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

Comments on Preferred Values

The new data of Toohey *et al.*[4] agree well with the previous work of Bemand *et al.*[3] at 298 K but shows a small negative temperature dependence over a similar range to that which Bemand *et al.* saw little change in k. The preferred value is the average of the 298 K values from these two studies and the temperature dependence of Toohey is accepted but with error limits covering the possibility that k is independent of temperature. Earlier work in Refs. 2 and 5 is rejected following the recommendation of Watson[6] and Bemand *et al.*[3]

References

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[8] NASA Evaluation No. 8, 1987 (see References in Introduction).

$HO + HCl \rightarrow H_2O + Cl$

$\Delta H^\circ = -67.5\ \mathrm{kJ\ mol^{-1}}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.8 \pm 0.25) \times 10^{-13}$	298	Cannon *et al.*, 1984[1]	(a)
$(2.94 \pm 0.48) \times 10^{-12} \exp[-(446 \pm 32)/T]$	300–700	Husain, Plane, and Xiang, 1984[2]	(b)
$(6.7 \pm 0.46) \times 10^{-13}$	298		
$(4.6 \pm 0.3) \times 10^{-12} \exp[-(500 \pm 60)/T]$	240–295	Molina, Molina, and Smith, 1984[3]	(c)
$(8.5 \pm 0.4) \times 10^{-13}$	298		
$(2.1 \pm 0.2) \times 10^{-12} \exp[-(285 \pm 48)/T]$	258–334	Keyser, 1984[4]	(d)
$(7.9 \pm 0.4) \times 10^{-13}$	298		
$(2.4 \pm 0.2) \times 10^{-12} \exp[-(327 \pm 28)/T]$	240–363	Ravishankara *et al.*, 1985[5]	(e)
$(8.01 \pm 0.44) \times 10^{-13}$	298		
Reviews and Evaluations			
$2.8 \times 10^{-12} \exp(-425/T)$	210–460	CODATA, 1984[6]	(f)
$2.6 \times 10^{-12} \exp(-350/T)$	200–300	NASA, 1987[7]	(g)

Comments

(a) Flash photolysis–laser-induced fluorescence study.

(b) Flash photolysis of H_2O–HO decay by time-resolved resonance fluorescence.

(c) Flash photolysis–HO decay by both resonance fluorescence and resonance absorption technique (298 K only).

(d) Discharge flow–resonance fluorescence study using high-pressure flow system.

(e) Flash photolysis of H_2O or laser photolysis (266 nm) of O_3/H_2O or H_2O_2 to produce HO. Time-resolved resonance fluorescence detection. Data obtained over a temperature range of 240–1055 K best represented by non-Arrhenius expression: $k = 4.5 \times 10^{-17} T^{1.65} \exp(112/T)$ cm^3 molecule^{-1} s^{-1}.

(f) Based on direct studies in Refs. 8–13.

(g) Based on data of Molina *et al.*,[3] Keyser,[4] and Ravishankara *et al.*,[5] which gave higher room-temperature values than earlier data.

Preferred Values

$k = 8.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.4 \times 10^{-12} \exp(-330/T)$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

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

Comments on Preferred Values

The most recent studies of Molina *et al.*,[3] Keyser,[4] and Ravishankara *et al.*,[5] which pay careful attention to the [HCl] present in the experiments, all show room-temperature values higher by about 20%–25% than the other studies. Ravishankara *et al.*[5] show that HCl losses can be a problem, leading to low k values, and this is a plausible cause of the discrepancy. The higher value, $k_1(298) = 8.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (average of the three studies) is the most reliable value. The preferred temperature-dependent expression for the range 200–300 K is obtained by weighted linear least-squares fit to the data from these three studies. Ravishankara *et al.*[5] give the following expression for the temperature range 240–1055 K: $k = 4.5 \times 10^{-17} T^{1.65} \exp(112/T)$ cm^3 molecule^{-1} s^{-1}, which gives a good description of the non-Arrhenius behavior.

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$HO + HOCl \rightarrow ClO + H_2O$

$\Delta H^\circ = -101$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.7\text{–}9.5)\times10^{-13}$	298	Ennis and Birks, 1988[1]	(a)
Reviews and Evaluations			
$3.0\times10^{-12}\exp(-150/T)$	200–300	CODATA, 1982[2]	(b)
$3.0\times10^{-12}\exp(-500/T)$	200–300	NASA, 1987[3]	(c)

Comments

(a) Discharge flow–mass spectrometric detection of HOCl. LIF detection of OH decay in excess HOCl. Correction made for reaction of OH with Cl_2($k = 5.5\times10^{-14}$ cm^3 molecule^{-1} s^{-1})[4] and with Cl_2O($k = 9.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} measured in the same study) and also secondary reactions that can complicate kinetics.

(b) By analogy with the $HO + H_2O_2$ reaction.

(c) Based on data from Ref. 1 and assuming the A factor is the same as that for the $HO + H_2O_2$ reaction.

Preferred Values

$k = 5.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.0\times10^{-12}\exp(-500/T)$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

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

Comments on Preferred Values

The only reported experimental value[1] has a large uncertainty. Following the NASA evaluation, the preferred value is based on the mid-range value of 5×10^{-13} cm^3 molecule^{-1} s^{-1} from this study and an A factor of 3.0×10^{-12} cm^3 molecule^{-1} s^{-1}, i.e., equal to that for the $HO + H_2O_2$ reaction.

References

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$HO + ClO \rightarrow HO_2 + Cl \quad (1)$
$\rightarrow HCl + O_2 \quad (2)$

$\Delta H^\circ(1) = -5$ kJ mol^{-1}
$\Delta H^\circ(2) = -234$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.0\pm1.4)\times10^{-12}\exp[(235\pm46)/T]$	219–373	Hills and Howard, 1984[1]	(a)
$(1.75\pm0.31)\times10^{-11}$	298		
$(1.19\pm0.09)\times10^{-11}$	243–298	Burrows, Wallington, and Wayne, 1984[2]	(b)
$(1.94\pm0.38)\times10^{-11}$	298	Poulet, Laverdet, and Le Bras, 1986[3]	(c)
Relative Rate Coefficients			
$k_1/k = 0.86\pm0.14$	298	Hills and Howard, 1984[1]	(a)
$k_1/k = 0.85\pm0.07$	243–298	Burrows, Wallington, and Wayne, 1984[2]	(b)
$k_1/k = 0.98\pm0.12$	298	Poulet, Laverdet, and Le Bras, 1986[3]	(c)
Reviews and Evaluations			
$9.2\times10^{-12}\exp(66/T)$	250–355	CODATA, 1984[4]	(d)
$1.0\times10^{-11}\exp(120/T)$	200–300	NASA, 1985[5]	(e)
$1.1\times10^{-11}\exp(120/T)$	200–300	NASA, 1987[6]	(f)

Comments

(a) Discharge flow–LMR detection of HO, ClO, and HO_2. Pseudo-first-order with $[ClO] \gg [HO]$. Branching ratio determined from HO_2 production after correction for secondary chemistry arising from $Cl + HO_2$ reaction.

(b) Discharge flow–resonance fluorescence detection of HO and indirectly for ClO and HO_2 after conversion to Cl and HO by titration with NO. Corrected HO_2 yield used to determine branching ratio.

(c) Discharge flow; laser-induced fluorescence detection of HO in presence of excess ClO. Molecular beam mass spectrometric detection of Cl, ClO, HCl, NO_2, OClO, etc. k determined by two direct methods, and one relative rate method in which $k(HO + OClO) = 6.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Ref. 5) was used as a reference reaction. Branching ratio determined from yield of HCl, after correction for HCl production from $Cl + HO_2$ reaction.

(d) Based on data of Ravishankara *et al.*[7] and Leu and Lin.[8]

(e) Based on data of Hills and Howard[1] and Burrows *et al.*[2]

(f) Based on data of Hills and Howard,[1] Burrows *et al.*,[2] and Poulet *et al.*[3] Earlier data[7,8] not used because [ClO] was not measured directly.

Preferred Values

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

$k = 1.1 \times 10^{-11} \exp(120/T)$ cm^3 molecule^{-1} s^{-1} over range 200–373 K.

$k_1/k = 0.98$.

Reliability

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

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

$\Delta (k_1/k) = {}^{+0.02}_{-0.13}$.

Comments on Preferred Values

The preferred value is based on the three recent studies[1-3] in which [ClO] was measured directly. The uncertainty reflects the differences in the 298 K values and the reported temperature coefficients. The measurements of the branching ratio for HCl formation based on measurement of this stable product[3] is more accurate since this is clearly the minor channel. However, the uncertainties do not allow the occurrence of this HCl channel to be eliminated completely.

References

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$HO + OClO \rightarrow HOCl + O_2$ (1)
$\rightarrow HO_2 + ClO$ (2)

$\Delta H^\circ(1) = -218$ kJ mol^{-1}
$\Delta H^\circ(2) = -24$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.50 \pm 0.75) \times 10^{-13} \exp[(804 \pm 114)/T]$	293–473	Poulet, Zagogianni, and Le Bras, 1986[1]	(a)
$(6.86 \pm 0.44) \times 10^{-12}$	298		
Reviews and Evaluations			
$4.5 \times 10^{-13} \exp(800/T)$	200–300	NASA, 1987[2]	(b)

Comments

(a) Discharge flow–EPR and LIF detection of pseudo-first-order decay of HO in excess OClO. HOCl product detected by modulated molecular beam mass spectrometry, calibrated using the $HO + Cl_2$ reaction as a source of HOCl. $k_1/k > 0.80$, and results suggest (1) in exclusive channel. Pressure = 0.5–1.4 Torr.

(b) Based on the single study of Poulet *et al.*[1]

Preferred Values

$k_1 = 7.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 4.5 \times 10^{-13} \exp(800/T)$ cm^3 molecule^{-1} s^{-1} over range 290–480 K.

$k_2 = 0$.

Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.

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

Comments on Preferred Values

The preferred values are based on the single experimental study of Poulet *et al.*[1] Indication of curvature in the Arrhenius plot dictates caution in extrapolation beyond the experimental range.

References

[1] G. Poulet, H. Zagogianni, and G. Le Bras, Int. J. Chem. Kinet. **18**, 847 (1986).
[2] NASA Evaluation No. 8, 1987 (see References in Introduction).

$HO + CH_3Cl \rightarrow H_2O + CH_2Cl$

$\Delta H^\circ = -80.7$ kJ mol^{-1}

$HO + CH_2FCl \rightarrow H_2O + CHFCl$
$HO + CHF_2Cl \rightarrow H_2O + CF_2Cl$

$\Delta H^\circ = -66.4$ kJ mol^{-1}

$HO + CHFCl_2 \rightarrow H_2O + CFCl_2$

$\Delta H^\circ = -92.2$ kJ mol^{-1}

Comments

The study of Jeong and Kaufman has been published.[1] A more recent publication of Jeong *et al.*[2] has provided corrected parameters for Arrhenius expressions and the modified Arrhenius expressions used. The previous recommendations[3] remain unaltered.

References

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[3] CODATA, Supplement II, 1984 (see References in Introduction).

$HO + CH_2Cl_2 \rightarrow H_2O + CHCl_2$

$\Delta H^\circ = -78.2$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.55 \pm 0.34) \times 10^{-13}$	296	Howard and Evenson, 1976[1]	(a)
$(1.45 \pm 0.20) \times 10^{-13}$	299	Perry, Atkinson, and Pitts, 1976[2]	(b)
$(4.27 \pm 0.63) \times 10^{-12} \exp[-(1094 \pm 81)/T]$	245–375	Davis *et al.*, 1976[3]	(b)
$(1.16 \pm 0.05) \times 10^{-13}$	298		
$(5.57 \pm 0.77) \times 10^{-12} \exp[-(1042 \pm 45)/T]$	251–455	Jeong and Kaufman, 1982[4]	(c)
$(1.53 \pm 0.10) \times 10^{-13}$	292		
Relative Rate Coefficients			
1.23×10^{-13}	298	Cox *et al.*, 1976[5]	(d)
$(2.7 \pm 1.0) \times 10^{-14}$	303	Butler, Solomon, and Snelson, 1978[6]	(e)
1.0×10^{-13}	300	Klöpffer *et al.*, 1986[7]	(f)
Reviews and Evaluations			
$4.5 \times 10^{-12} \exp(-1032/T)$	~220–300	NASA, 1985[8]	(g)
$8.54 \times 10^{-18} T^2 \exp(-500/T)$	245–455	Atkinson, 1986[9]	(h)
$4.7 \times 10^{-12} \exp(-1050/T)$	~220–300	NASA, 1987[10]	(g)

Comments

(a) Discharge flow–laser magnetic resonance detection of HO.

(b) Flash photolysis–resonance fluorescence detection of HO.

(c) Discharge flow–resonance fluorescence detection of HO. The Arrhenius expression and three-parameter equations given by Jeong and Kaufman[4] were subsequently revised.[11] The revised Arrhenius expression is given in the table. The experimental data were observed to exhibit non-Arrhenius behavior, and were best described by the three-parameter expression $k = 1.61 \times 10^{-19} T^{2.54} \exp(-370/T)$ cm^3 molecule^{-1} s^{-1}.

(d) Relative rate method. HO radicals generated by photolysis of HONO in 1 atm of air. Relative rate coefficients obtained from measurements of the rate of NO formation as a function of the HONO and organic concentrations. Placed on an absolute basis by use of $k(HO + CH_4) = 8.3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. Value uncertain by up to a factor of 2, due to the uncertainty in the number of molecules of NO oxidized following OH radical reaction.

(e) Relative rate method. HO radicals generated by photolysis of H_2O_2–O_2–N_2 mixtures (400 Torr total pressure) at ~300 nm. Rate coefficient obtained relative to those for the reactions of HO radicals with H_2O_2 and CO from a complex expression, and cannot be reevaluated to be consistent with more recent data for the reference reactions.

(f) Relative rate method. HO radicals generated by photolysis of HONO–air or NO–NO_2–organic–air mixtures in a chamber. No details of the reference compound used given.

(g) Derived from the absolute rate coefficient data of Howard and Evenson,[1] Perry *et al.*,[2] Davis *et al.*,[3] and Jeong and Kaufman.[4] A fit of these data to the three-parameter equation $k = CT^2 \exp(-D/T)$ resulted in

$k = 8.58\times10^{-18}T^2 \exp(-502/T)$ cm^3 molecule^{-1} s^{-1} over the range 245–455 K. The cited 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 $B = D + 2T$.

(h) Derived from the absolute rate coefficient data of Howard and Evenson,[1] Perry *et al.*,[2] Davis *et al.*,[3] and Jeong and Kaufman,[4] using the three-parameter equation $k = CT^2 \exp(-D/T)$.

Preferred Values

$k = 1.4\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.4\times10^{-12} \exp(-1030/T)$ cm^3 molecule^{-1} s^{-1} over the range ~240–300 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are derived from the absolute rate coefficients of Howard and Evenson,[1] Perry *et al.*,[2] Davis *et al.*,[3] and Jeong and Kaufman.[4] A fit of these data to the three-parameter equation $k = CT^2 \exp(-D/T)$ yields $k = 8.54\times10^{-18}T^2 \exp(-500/T)$ cm^3 molecule^{-1} s^{-1} over the range 245–455 K.[9] 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 preferred expression is essentially identical to those in the NASA evaluations.[8,10]

References

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[11] K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. **88**, 1222 (1984).

$HO + CHCl_3 \rightarrow H_2O + CCl_3$

$\Delta H^\circ = -98.7$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.01 \pm 0.15)\times10^{-13}$	296	Howard and Evenson, 1976[1]	(a)
$(4.69 \pm 0.71)\times10^{-12} \exp[-(1134 \pm 108)/T]$	245–375	Davis *et al.*, 1976[2]	(b)
$(1.14 \pm 0.07)\times10^{-13}$	298		
$(5.63 \pm 0.68)\times10^{-12} \exp[-(1183 \pm 45/T]$	249–487	Jeong and Kaufman, 1982[3]	(c)
$(1.01 \pm 0.065)\times10^{-13}$	298		
Relative Rate Coefficients			
2.0×10^{-13}	298	Cox *et al.*, 1976[4]	(d)
3.0×10^{-13}	300	Klöpffer *et al.*, 1986,[5] 1988[6]	(e)
Reviews and Evaluations			
$3.3\times10^{-12} \exp(-1034/T)$	~220–300	NASA, 1985[7]	(f)
$6.30\times10^{-18}T^2 \exp(-504/T)$	245–487	Atkinson, 1986[8]	(g)
$3.4\times10^{-12} \exp(-1050/T)$	~220–300	NASA, 1987[9]	(f)

Comments

(a) Discharge flow–laser magnetic resonance detection of HO.

(b) Flash photolysis–resonance fluorescence detection of HO.

(c) Discharge flow–resonance fluorescence detection of HO. The Arrhenius expression and three-parameter fit given by Jeong and Kaufman[3] were subsequently revised.[10] The revised Arrhenius expression is given in the table. The experimental data were observed to exhibit non-Arrhenius behavior, and were best described by the three-parameter expression $k = 6.91\times10^{-20}T^{2.65} \exp(-262/T)$ cm^3 molecule^{-1} s^{-1}.

(d) Relative rate method. HO radicals generated by photolysis of HONO in air in 1 atm of air. Relative rate coefficients obtained from measurement of the rate of NO formation as a function of the HONO and organic concentrations. Placed on an absolute basis by use of $k(HO + CH_4) = 8.3\times10^{-15}$ cm^3 molecule^{-1} s^{-1}. Value uncertain by up to a factor of 2, due to uncertainty in the number of NO molecules oxidized following OH radical reaction.

(e) Relative rate method. HO radicals generated by photolysis of HONO–air mixtures in a chamber. No details given concerning the reference compound used.

(f) Derived using the absolute rate coefficient data of Howard and Evenson,[1] Davis *et al.*,[2] and Jeong and Kaufman.[3] A fit of these data to the three-parameter equation $k = CT^2 \exp(-D/T)$ resulted in $k = 6.3\times10^{-18}T^2 \exp(-504/T)$ cm^3 molecule^{-1} s^{-1} over the range 245–487 K. The cited 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 $B = D + 2T$.

(g) Derived using the absolute rate coefficient data of Howard and Evenson,[1] Davis *et al.*,[2] and Jeong and Kaufman.[3] These data were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, yielding an identical expression to the NASA[7,9] three-parameter expression.

Preferred Values

$k = 1.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.3\times10^{-12} \exp(-1030/T)$ cm^3 molecule^{-1} s^{-1} over the range 240–300 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are derived using the absolute rate coefficient data of Howard and Evenson,[1] Davis *et al.*,[2] and Jeong and Kaufman,[3] which are in excellent agreement. A fit of these data to the three-parameter equation $k = CT^2 \exp(-D/T)$ yields $k = 6.30\times10^{-18}T^2 \exp(-504/T)$ cm^3 molecule^{-1} s^{-1} over the range 245–487 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] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).

[2] D. D. Davis, G. Machado, B. C. Conaway, Y. Oh, and R. T. Watson, J. Chem. Phys. **65**, 1268 (1976).

[3] K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).

[4] R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, Atmos. Environ. **10**, 305 (1976).

[5] W. Klöpffer, R. Frank, E.-G. Kohl, and F. Haag, Chem-Ztg. **110**, 57 (1986).

[6] W. Klöpffer, F. Haag, E.-G. Kohl, and R. Frank, Ecotoxicol. Environ. Safety XX, XXX (1988).

[7] NASA Evaluation No. 7, 1985 (see References in Introduction).

[8] R. Atkinson, Chem. Rev. **86**, 69 (1986).

[9] NASA Evaluation No. 8, 1987 (see References in Introduction).

[10] K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. **88**, 1222 (1984).

$HO + CFCl_3 \rightarrow HOCl + CFCl_2$

$\Delta H^\circ = 71.6$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<1\times10^{-15}$	297–424	Atkinson, Hansen, and Pitts, 1975[1]	(a)
$<5\times10^{-16}$	296	Howard and Evenson, 1976[2]	(b)
$<5\times10^{-16}$	480	Chang and Kaufman, 1977[3]	(c)
$<1\times10^{-15}$	293	Clyne and Holt, 1979[4]	(d)
Relative Rate Coefficients			
$<5\times10^{-17}$	298	Cox *et al.*, 1976[5]	(e)
Reviews and Evaluations			
$<1.0\times10^{-12} \exp(-3650/T)$	<480	NASA, 1985[6]	(f)
$<5.0\times10^{-18}$	298		
$<1.0\times10^{-12} \exp(-3700/T)$	<480	NASA, 1987[7]	(f)
$<5\times10^{-18}$	298		

Comments

(a) Flash photolysis–resonance fluorescence detection of HO.

(b) Discharge flow–laser magnetic resonance detection of HO.

(c) Discharge flow–resonance fluorescence detection of HO. The upper limit rate coefficient obtained at 480 K was combined with an estimated Arrhenius preexponential factor of 10^{-12} cm^3 molecule^{-1} s^{-1} to derive an estimated Arrhenius activation energy of $\geqslant$29 kJ mol^{-1}.

(d) Discharge flow–resonance fluorescence detection of HO.

(e) Relative rate study. HO radicals generated by photolysis of HONO–air mixtures at 1 atm total pressure in a chamber. The relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based upon the lack of NO formation as a function of added $CFCl_3$ and $k(HO + CH_4) = 8.3\times10^{-15}$ cm^3 molecule^{-1} s^{-1}, the upper limit given in the table is obtained.

(f) Derived by assuming an Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} and using the upper limit to the rate coefficient measured by Chang and Kaufman at 480 K.[3]

Preferred Values

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

$k < 1 \times 10^{-12}$ exp($-3650/T$) cm^3 molecule^{-1} s^{-1} over the range 250–480 K.

Comments on Preferred Values

Similar to the NASA evaluations.[6,7] Based upon an estimated Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} and the upper limit to the rate coefficient determined at 480 K in the absolute rate study of Chang and Kaufman.[3] This yields $k < 1 \times 10^{-12}$ exp($-3650/T$) cm^3 molecule^{-1} s^{-1}, and is consistent with the lack of reaction observed by Cox *et al.*[5] in their relative rate study.

References

[1] R. Atkinson, D. A. Hansen, and J. N. Pitts, Jr., J. Chem. Phys. **63**, 1703 (1975).
[2] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[3] J. S. Chang and F. Kaufman, Geophys. Res. Lett. **4**, 192 (1977).
[4] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2 **75**, 569 (1979).
[5] R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, Atmos. Environ. **10**, 305 (1976).
[6] NASA Evaluation No. 7, 1985 (see References in Introduction).
[7] NASA Evaluation No. 8, 1987(see References in Introduction).

$HO + CF_2Cl_2 \rightarrow HOCl + CF_2Cl$

$\Delta H^\circ = 107.0$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$< 1 \times 10^{-15}$	297–424	Atkinson, Hansen, and Pitts, 1975[1]	(a)
$< 4 \times 10^{-16}$	296	Howard and Evenson, 1976[2]	(b)
$< 6 \times 10^{-16}$	478	Chang and Kaufman, 1977[3]	(c)
$< 1 \times 10^{-15}$	293	Clyne and Holt, 1979[4]	(d)
Relative Rate Coefficients			
$< 1.2 \times 10^{-16}$	298	Cox *et al.*, 1976[5]	(e)
Reviews and Evaluations			
$< 1 \times 10^{-12}$ exp($-3560/T$)	<478	NASA, 1985[6]	(f)
$< 6.5 \times 10^{-18}$	298		
$< 1 \times 10^{-12}$ exp($-3600/T$)	<478	NASA, 1987[7]	(f)
$< 6.0 \times 10^{-18}$	298		

Comments

(a) Flash photolysis–resonance fluorescence detection of HO.

(b) Discharge flow–laser magnetic resonance detection of HO.

(c) Discharge flow–resonance fluorescence detection of HO. The upper limit rate coefficient obtained at 478 K was combined with an estimated Arrhenius preexponential factor of 10^{-12} cm^3 molecule^{-1} s^{-1} to derive an estimated Arrhenius activation energy of $\geqslant 29$ kJ mol^{-1}.

(d) Discharge flow–resonance fluorescence detection of HO.

(e) Relative rate study. HO radicals generated by photolysis of HONO–air mixtures at 1 atm total pressure in a chamber. The relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based upon the lack of NO formation as a function of added CF_2Cl_2 and a rate coefficient of $k(HO + CH_4) = 8.3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, the upper limit given in the table is obtained.

(f) Derived by assuming an Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} and using the upper limit to the rate coefficient measured by Chang and Kaufman at 478 K.[3]

Preferred Values

$k < 7 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k < 1 \times 10^{-12}$ exp($-3540/T$) cm^3 molecule^{-1} s^{-1} over the range 250–478 K.

Comments on Preferred Values

Similar to the NASA evaluations.[6,7] Based upon an estimated Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} and the upper limit to the rate coefficient determined at 478 K in the absolute rate study of Chang and Kaufman.[3] This yields $k < 1 \times 10^{-12}$ exp($3540/T$) cm^3 molecule^{-1} s^{-1}, and is consistent with the lack of reaction observed by Cox *et al.*[5] in their relative rate study.

References

[1] R. Atkinson, D. A. Hansen, and J. N. Pitts, Jr., J. Chem. Phys. **63**, 1703 (1975).
[2] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[3] J. S. Chang and F. Kaufman, Geophys. Res. Lett. **4**, 192 (1977).
[4] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2 **75**, 569 (1979).
[5] R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, Atmos. Environ. **10**, 305 (1976).
[6] NASA Evaluation No. 7, 1985 (see References in Introduction).
[7] NASA Evaluation No. 8, 1987 (see References in Introduction).

$HO + CCl_4 \rightarrow HOCl + CCl_3$

$\Delta H^\circ = 58.0$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<4\times10^{-16}$	296	Howard and Evenson, 1976[1]	(a)
$<1\times10^{-15}$	293	Clyne and Holt, 1979[2]	(b)
Relative Rate Coefficients			
$<1.2\times10^{-16}$	298	Cox *et al.*, 1976[3]	(c)

Comments

(a) Discharge flow–laser magnetic resonance detection of HO.

(b) Discharge flow–resonance fluorescence detection of HO.

(c) Relative rate study. HO radicals generated by photolysis of HONO–air mixtures at 1 atm total pressure in a chamber. The relative rate coefficients were obtained from measurement of the rates of NO formation as a function of the HONO and organic concentrations. Based upon the lack of NO formation as a function of added CCl_4 and a rate coefficient of $k(HO + CH_4) = 8.3\times10^{-15}$ cm^3 molecule^{-1} s^{-1}, the upper limit given in the table is obtained.

Preferred Values

$k < 4\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k < 1\times10^{-12} \exp(-2320/T)$ cm^3 molecule^{-1} s^{-1}.

Comments on Preferred Values

The 298 K rate coefficient is the upper limit measured by Howard and Evenson,[1] which is supported by the data of Clyne and Holt[2] and Cox *et al.*[3] Assuming an Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1}, this leads to the upper limit to the Arrhenius expression given.

References

[1] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[2] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2 **75**, 569 (1979).
[3] R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, Atmos. Environ. **10**, 305 (1976).

$HO + C_2HCl_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.11×10^{-12}	305	Kirchner, 1983[1]	(a)
Relative Rate Coefficients			
$(2.86\pm0.40)\times10^{-12}$	296	Edney, Kleindienst, and Corse, 1986[2]	(b)
2.9×10^{-12}	300	Klöpffer *et al.*, 1986,[3] 1988[4]	(c)
Reviews and Evaluations			
$5.0\times10^{-13}\exp(445/T)$	234–420	CODATA, 1984[5]	(d)
$5.0\times10^{-13}\exp(445/T)$	234–420	NASA, 1985[6]	(d)
$5.6\times10^{-13}\exp(427/T)$	234–420	Atkinson, 1986[7]	(e)
$4.9\times10^{-13}\exp(450/T)$	234–420	NASA, 1987[8]	(d)

Comments

(a) Discharge flow–mass spectroscopic detection of HO.

(b) Relative rate technique. HO radicals generated by the photolysis of CH_3ONO–NO–air mixtures in a chamber at atmospheric pressure. Rate coefficient determined relative to that for HO + n-butane, using $k(HO + n\text{-butane}) = 2.52\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[7] Secondary reactions involving Cl atoms formed from the $HO + C_2HCl_3$ reaction were observed to occur; the effects of these secondary reactions were circumvented by extrapolating the experimental data to $([C_2HCl_3]/[n\text{-butane}])_{\text{initial}} = 0$.

(c) Relative rate method. HO radicals generated by photolysis of NO–NO_2–organic–air mixtures at atmospheric pressure. Relative decay rates of trichloroethene and toluene were measured, and placed on an absolute basis by using $k(\text{HO} + \text{toluene}) = 6.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(d) The 298 K value derived from the mean of the values reported by Howard[9] and Chang and Kaufman.[10] The Arrhenius parameters are those of Chang and Kaufman[10] with the A factor being reduced to yield the preferred value at 298 K.

(e) Derived from the data of Howard[9] and Chang and Kaufman[10] and unpublished data of Davis *et al.* (cited in Refs. 9 and 10).

Preferred Values

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

$k = 5.0 \times 10^{-13} \exp(445/T)$ cm^3 molecule^{-1} s^{-1} over the range 230–420 K.

Reliability

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

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

Comments on Preferred Values

Unchanged from the CODATA, 1984 evaluation.[4] The 298 K value is derived from the mean of the values of Howard[9] and Chang and Kaufman.[10] The Arrhenius parameters are those of Chang and Kaufman,[10] with the A factor reduced to yield the preferred value at 298 K. The uncertainties in the preferred Arrhenius activation energy have been decreased, on the basis of the data for the HO + C_2Cl_4 reaction. The room-temperature rate coefficients reported by Kirchner,[1] Edney *et al.*,[2] and Klöpffer *et al.*,[3,4] which are not used in the derivation of the preferred values, are nevertheless in agreement with the preferred values.

References

[1] K. Kirchner, Chimia **37**, 1 (1983).
[2] E. O. Edney, T. E. Kleindienst, and E. W. Corse, Int. J. Chem. Kinet. **18**, 1355 (1986).
[3] W. Klöpffer, R. Frank, E.-G. Kohl, and F. Haag, Chem-Ztg. **110**, 57 (1986).
[4] W. Klöpffer, F. Haag, E.-G. Kohl, and R. Frank, Ecotoxicol. Environ. Safety **15**, 298 (1988).
[5] CODATA, Supplement II, 1984 (see References in Introduction).
[6] NASA Evaluation No. 7, 1985 (see References in Introduction).
[7] R. Atkinson, Chem. Rev. **86**, 69 (1986).
[8] NASA Evaluation No. 8, 1987 (see References in Introduction).
[9] C. J. Howard, J. Chem. Phys. **65**, 4771 (1976).
[10] J. S. Chang and F. Kaufman, J. Chem. Phys. **66**, 4989 (1977).

HO + C_2Cl_4 → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.53 \times 10^{-12} \exp(-1034/T)$	275–385	Kirchner, 1983[1]	(a)
1.79×10^{-13}	305		
Reviews and Evaluations			
$9.4 \times 10^{-12} \exp(-1200/T)$	297–420	CODATA, 1984[2]	(b)
$9.4 \times 10^{-12} \exp(-1200/T)$	297–420	NASA, 1985[3]	(b)
$9.64 \times 10^{-12} \exp(-1209/T)$	297–420	Atkinson, 1986[4]	(c)
$9.4 \times 10^{-12} \exp(-1200/T)$	297–420	NASA, 1987[5]	(b)

Comments

(a) Discharge flow–mass spectroscopic detection of HO. Few details are given.

(b) The 298 K value derived from the mean of the values reported by Howard,[6] and Chang and Kaufman.[7] The Arrhenius parameters are those of Chang and Kaufman.[7]

(c) Derived from the data of Howard[6] and Chang and Kaufman[7] and the unpublished 298 K rate coefficient of Davis *et al.* (cited in Refs. 6 and 7).

Preferred Values

$k = 1.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.4 \times 10^{-12} \exp(-1200/T)$ cm^3 molecule^{-1} s^{-1} over the range 300–420 K.

Reliability

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

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

Comments on Preferred Values

Unchanged from the CODATA, 1984 evaluation.[3] The 298 K value is derived from the mean of the values of Howard[6] and Chang and Kaufman.[7] The Arrhenius parameters are those of Chang and Kaufman.[7] The Arrhenius expression and 305 K rate coefficient reported by Kirchner,[1] which are not used in the derivation of the preferred values, are in reasonable agreement with the preferred values.

References

[1] K. Kirchner, Chimia **37**, 1 (1983).
[2] CODATA, Supplement II, 1984 (see References in Introduction).
[3] NASA Evaluation No. 7, 1985 (see References in Introduction).
[4] R. Atkinson, Chem. Rev. **86**, 69 (1986).
[5] NASA Evaluation No. 8, 1987 (see References in Introduction).
[6] C. J. Howard, J. Chem. Phys. **65**, 4771 (1976).
[7] J. S. Chang and F. Kaufman, J. Chem. Phys. **66**, 4989 (1977).

$HO + CH_3CF_2Cl \rightarrow H_2O + CH_2CF_2Cl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.83 \pm 0.42) \times 10^{-15}$	296	Howard and Evenson, 1976[1]	(a)
$(1.15 \pm 0.15) \times 10^{-12} \exp[-(1748 \pm 30)/T]$	273–375	Watson *et al.*, 1977[2]	(b)
$(3.22 \pm 0.48) \times 10^{-15}$	298		
$(1.8 \pm 0.5) \times 10^{-12} \exp[-(1790 \pm 150)/T]$	293–373	Handwerk and Zellner, 1978[3]	(c)
$(3.7 \pm 0.7) \times 10^{-15}$	293		
$(3.3^{+4.3}_{-1.9}) \times 10^{-12} \exp[-(1800 \pm 300)/T]$	293–417	Clyne and Holt, 1979[4]	(d)
$(8.4 \pm 1.8) \times 10^{-15}$	293		
$(4.63 \pm 1.73) \times 10^{-15}$	297	Paraskevopoulos, Singleton, and Irwin, 1981[5]	(c)
Reviews and Evaluations			
$2.05 \times 10^{-18} T^2 \exp(-1171/T)$	273–375	Atkinson, 1986[6]	(e)
$1.5 \times 10^{-12} \exp(-1800/T)$	273–375	NASA, 1987[7]	(f)

Comments

(a) Discharge flow–laser magnetic resonance detection of HO.

(b) Flash photolysis–resonance fluorescence detection of HO.

(c) Flash photolysis–resonance absorption detection of HO.

(d) Discharge flow–resonance fluorescence detection of HO.

(e) Derived from a least–squares analysis of the rate coefficient data of Howard and Evenson,[1] Watson *et al.*,[2] Handwerk and Zellner,[3] and Paraskevopoulos *et al.*[5] The data of Clyne and Holt[4] were not used in the evaluation.

(f) The room-temperature rate constant was the mean of the rate coefficients measured by Howard and Evenson,[1] Watson *et al.*,[2] Handwerk and Zellner,[3] and Paraskevopoulos *et al.*[5] The temperature dependence was derived from those measured by Watson *et al.*,[2] Handwerk and Zellner,[3] and Clyne and Holt,[4] with the A factor being adjusted to fit the 298 K value.

Preferred Values

$k = 3.6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

$k = 1.6 \times 10^{-12} \exp(-1820/T)$ cm^3 molecule^{-1} s^{-1} over the range 270–380 K.

Reliability

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

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

Comments on Preferred Values

Derived from a least-squares analysis of the rate coefficients of Howard and Evenson,[1] Watson *et al.*,[2] Handwerk and Zellner,[3] and Paraskevopoulos *et al.*[5]

References

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

[2] R. T. Watson, G. Machado, B. Conaway, S. Wagner, and D. D. Davis, J. Phys. Chem. **81**, 256 (1977).

[3] V. Handwerk and R. Zellner, Ber. Bunsenges. Phys. Chem. **82**, 1161 (1978).

[4] M. A. A. Clyne and P. M. Holt, J. Chem. Soc., Faraday Trans. 2 **75**, 582 (1979).

[5] G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, J. Phys. Chem. **85**, 561 (1981).

[6] R. Atkinson, Chem. Rev. **86**, 69 (1986).

[7] NASA Evaluation No. 8, 1987 (see References in Introduction).

$HO + CHFClCF_3 \rightarrow H_2O + CFClCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.24 \pm 0.19) \times 10^{-14}$	296	Howard and Evenson, 1976[1]	(a)
$(6.13 \pm 0.4) \times 10^{-13} \exp[-(1244 \pm 90)/T]$	250–375	Watson *et al.*, 1979[2]	(b)
$(9.4 \pm 0.3) \times 10^{-15}$	301		
Reviews and Evaluations			
$6.38 \times 10^{-13} \exp(-1233/T)$	250–375	Atkinson, 1986[3]	(c)
$7.2 \times 10^{-13} \exp(-1250/T)$	250–375	NASA, 1987[4]	(d)

Comments

(a) Discharge flow–laser magnetic resonance detection of HO.

(b) Flash photolysis–resonance fluorescence detection of HO.

(c) Derived from a least-squares analysis of the rate coefficients of Howard and Evenson[1] and Watson *et al.*[2]

(d) Room-temperature rate coefficient is the mean of those determined by Howard and Evenson[1] and Watson *et al.*[2] The temperature dependence is that of Watson *et al.*[2]

Preferred Values

$k = 1.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.4 \times 10^{-13} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} over the range 250–380 K.

Relability

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

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

Comments on Preferred Values

Accepts the evaluation of Atkinson,[3] which is very similar to the NASA evaluation.[4]

References

[1] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 4303 (1976).
[2] R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, Int. J. Chem. Kinet. **11**, 187 (1979).
[3] R. Atkinson, Chem. Rev. **86**, 69 (1986).
[4] NASA Evaluation No. 8, 1987 (see References in Introduction).

$HO + CH_2ClCF_2Cl \rightarrow H_2O + CHClCF_2Cl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3^{+6}_{-1}) \times 10^{-12} \exp[-(1578^{+400}_{-230})/T]$	250–350	Watson *et al.*, 1979[1]	(a)
1.5×10^{-14}	298		
$5.54 \times 10^{-26} T^{4.58 \pm 1.13}$	249–473	Jeong *et al.*, 1984[2]	(b)
$(2.42 \pm 0.16) \times 10^{-14}$	297		
Reviews and Evaluations			
$3.4 \times 10^{-12} \exp(-1600/T)$	250–350	NASA, 1987[2]	(c)

Comments

(a) Flash photolysis–resonance fluorescence detection of HO. Measured rate constants yielded the Arrhenius expression $k = 1.87 \times 10^{-12} \exp(-1351/T)$ cm^3 molecule^{-1} s^{-1}, $k = (1.9 \pm 0.2) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K. However, chemical analysis showed the presence of reactive impurities, and the Arrhenius expression corrected to take into account the contributions of these impurities on the HO radial decay rates is given in the table.

(b) Discharge flow–resonance fluorescence detection of HO.

(c) Derived from the corrected data of Watson *et al.*[1]

Preferred Values

$k = 1.5 \times 10^{-14}$ cm^2 molecule^{-1} s^{-1} at 298 K.

$k = 3.0 \times 10^{-12} \exp(-1580/T)$ cm^3 molecule^{-1} s^{-1} over the range 250–350 K.

Reliability

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

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

Comments on Preferred Values

Accepts the corrected data of Watson *et al.*[2] and is essentially identical to the NASA evaluation.[3] The rate coefficients of Jeong *et al.*[2] are higher, especially at < 300 K.

References

[1] R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis Int. J. Chem. Kinet. **11**, 187 (1979).
[2] K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and K. Kaufman, J. Phys. Chem. **88**, 1222 (1984).
[3] NASA Evaluation No. 8, 1987 (see References in Introduction).

$HO + CHCl_2CF_3 \rightarrow H_2O + CCl_2CF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.84 \pm 0.43) \times 10^{-14}$	296	Howard and Evenson, 1976[1]	(a)
$(1.4 \pm 0.4) \times 10^{-12} \exp[-(1102^{+157}_{-106})/T]$	245–375	Watson *et al.*, 1979[2]	(b)
3.5×10^{-14}	298		
$(1.12 \pm 0.05) \times 10^{-12} \exp[-(1000 \pm 100)/T]$	293–429	Clyne and Holt, 1979[3]	(c)
$(3.86 \pm 0.19) \times 10^{-14}$	293		
Reviews and Evaluations			
$1.16 \times 10^{-12} \exp(-1056/T)$	245–375	Atkinson, 1986[4]	(d)
$1.1 \times 10^{-12} \exp(-1050/T)$	245–375	NASA, 1987[5]	(e)

Comments

(a) Discharge flow–laser magnetic resonance detection of HO.

(b) Flash photolysis–resonance fluorescence detection of HO. Measured rate coefficients corrected to take into account the presence of reactive impurities. This correction was small.

(c) Discharge flow–resonance fluorescence detection of HO.

(d) Derived from least-squares analysis of the rate coefficients of Howard and Evenson[1] and Watson *et al.*[2] The data of Clyne and Holt[3] were not considered in evaluating this reaction.

(e) Room-temperature rate coefficient is the mean of those of Howard and Evenson[1] and Watson *et al.*[2] The temperature dependence is that of Watson *et al.*[2]

Preferred Values

$k = 3.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.2 \times 10^{-12} \exp(-1060/T)$ cm^3 molecule^{-1} s^{-1} over the range 245–375 K.

Reliability

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

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

Comments on Preferred Values

Accepts the evaluation of Atkinson,[4] which is very similar to the recent NASA evaluation.[5]

References

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

[2] R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, Int. J. Chem. Kinet. **11**, 187 (1979).

[3] M. A. A. Clyne and P. M. Holt, J. Chem. Soc., Faraday Trans 2 **75**, 582 (1979).

[4] R. Atkinson, Chem. Rev. **86**, 69 (1986).

[5] NASA Evaluation No. 8, 1987 (see References in Introduction).

$NO_3 + C_2HCl_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(2.9 \pm 0.5) \times 10^{-16}$	298	Atkinson, Aschmann, and Goodman, 1987	(a)

Comments

(a) Derived from a relative rate method, by monitoring the relative decay rates of C_2HCl_3 and C_2H_4 in N_2O_5–NO_2–organic–air mixtures at 1 atm total pressure of air. The observed decay rates yielded $k(NO_3 + C_2HCl_3)/k(NO_3 + C_2H_4) = 1.37 \pm 0.08$. This rate coefficient ratio is placed on an absolute basis by use of $k(NO_3 + C_2H_4) = (2.1 \pm 0.3) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}.[2]

Preferred Values

$k = 2.9 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is derived from the relative rate coefficients measured by Atkinson, Aschmann, and Goodman[1] as discussed in comment (a) above. The cited uncertainty limits have been increased.

References

[1] R. Atkinson, S. M. Aschmann, and M. A. Goodman, Int. J. Chem. Kinet. **19**, 299 (1987).
[2] R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., J. Phys. Chem. **92**, 3454 (1988).

$NO_3 + C_2Cl_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$< 6 \times 10^{-17}$	298	Atkinson, Aschmann, and Goodman, 1987[1]	(a)

Comments

(a) Derived from a relative rate method, by monitoring the relative decay rates of C_2Cl_4 and C_2H_4 in N_2O_5–NO_2–organic–air mixtures at 1 atm total pressure of air. The observations yielded $k(NO_3 + C_2Cl_4)/k(NO_3 + C_2H_4) < 0.25$. This upper limit to the rate coefficient ratio is placed on an absolute basis by use of $k(NO_3 + C_2H_4) = (2.1 \pm 0.3) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}.[2]

Preferred Values

$k < 1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is derived from the relative rate coefficients measured by Atkinson, Aschmann, and Goodman[1] as discussed in comment (a) above. The upper limit to the rate coefficient has been increased over that derived from the relative rate coefficient data.[1]

References

[1] R. Atkinson, S. M. Aschmann, and M. A. Goodman, Int. J. Chem. Kinet. **19**, 299 (1987).
[2] R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., J. Phys. Chem. **92**, 3454 (1988).

$ClO + HO_2 \rightarrow HOCl + O_2$ (1)
$\rightarrow HCl + O_3$ (2)

$\Delta H^\circ(1) = -195$ kJ mol^{-1}
$\Delta H^\circ(2) = -66$ 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			
$(6.2 \pm 1.5) \times 10^{-12}$	308	Cattell and Cox, 1986[1]	(a)
Reviews and Evaluations			
$4.6 \times 10^{-13} \exp(710/T)$	200–300	CODATA, 1982[2]	(b)
$4.8 \times 10^{-13} \exp(700/T)$	200–300	NASA, 1987[3]	(c)

Comments

(a) Molecular modulation—UV absorption study. ClO produced in presence of excess HO_2 from $Cl + HO_2$ reaction in photolysis of Cl_2–H_2–O_2–N_2 mixtures. $[HO_2]$ calculated using UV absorption cross-section $\sigma = 3.5 \times 10^{-18}$ cm^2 molecule^{-1} at 200 nm. k independent of pressure in range 50–760 Torr at 308 K.

(b) Based on measurements of Reimann and Kaufman,[4] Stimpfle *et al.*,[5] Leck *et al.*,[6] and Burrows and Cox.[7]

(c) As (b) but with data of Cattell and Cox[1] included.

Preferred Values

$k = 5.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.6 \times 10^{-13} \exp(710/T)$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

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

Comments on Preferred Values

The new data are in good agreement with the earlier measurements[4–7] and the absence of pressure dependence excludes a possible addition channel. The lowest upper limit for HCl formation via channel (2) is $k_2 \leqslant 2.0\times10^{-14}$ cm^3 s^{-1} at 298 K.[7] The preferred value over the range 200–300 K is unchanged.

References

[1] F. C. Cattell and R. A. Cox, J. Chem. Soc. Faraday 2 **82**, 1413 (1986).

[2] CODATA Supplement I, 1982 (see References in Introduction).

[3] NASA Evaluation No. 8, 1987 (see References in Introduction).

[4] B. Reimann and K. Kaufman, J. Chem. Phys., **69**, 2925 (1978).

[5] R. Stimpfle, R. Perry, and C. J. Howard, J. Chem. Phys., **71**, 5183 (1979).

[6] T. J. Leck, J. E. Cook, and J. W. Birks, J. Chem. Phys. **72**, 2364 (1980).

[7] J. P. Burrow and R. A. Cox, J. Chem. Soc. Faraday 1 **77**, 2465 (1981).

$ClO + O_2(^1\Delta) \rightarrow ClO_3$

$\Delta H^\circ = -41$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<3\times10^{-15}[O_2(^1\Delta)]$	289	Handwerk and Zellner, 1986[1]	(a)

Comments

(a) $O_2(^1\Delta)$ from microwave discharge in O_2; ClO from flash photolysis of Cl_2O in a slow flow system and measured by long-path UV absorption. Up to 1.4×10^{15} cm^{-3} $O_2(^1\Delta)$.

Preferred Value

$k < 3.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

The assumed product of this reaction is symmetrical $ClO_3(^2A_1)$. The corresponding reaction between ClO and ground state $O_2(^3\Sigma_g^-)$ is endothermic ($\Delta H^\circ = 52$ kJ mol^{-1}). The upper limit value at 298 K is consistent with a significant activation barrier, which is expected for the reaction that involves considerable rearrangement of the reactant molecules.

References

[1] V. Handwerk and R. Zellner, Ber. Bunsenges Phys. Chem. **90**, 92 (1986).

$ClO + NO_2 + M \rightarrow ClONO_2 + M$

$\Delta H^\circ = -109$ kJ mol^{-1}

Comment

Wallington and Cox,[1] using modulated photolysis of OClO–NO_2–N_2 mixtures with ClO detection by UV absorption, reported $k_0 = (1.40 \pm 0.07)\times10^{-31}$ cm^6 molecule^{-2} s^{-1} in good agreement with previous studies. Burrows *et al.*[2] used matrix isolation FTIR spectroscopy to study the products of the gas-phase reaction of ClO with NO_2. The yield of chlorine nitrate was found to be 0.93 ± 0.20 at 22 Torr pressure and 253–298 K. No evidence was found for any other products, including isomers of $ClNO_3$. No change in the preferred values is recommended.

References

[1] T. J. Wallington and R. A. Cox, J. Chem. Soc. Faraday 2 **82**, 275 (1986).

[2] J. P. Burrows, D. W. T. Griffiths, G. K. Moortgat, and G. S. Tyndall, J. Phys. Chem. **89**, 266 (1985).

$ClO + NO_3 \rightarrow ClOO + NO_2$ (1)
$\rightarrow OClO + NO_2$ (2)

ΔH° (1) = -46.6 kJ mol^{-1}
ΔH° (2) = -40.6 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			
$(4.0 \pm 1.7)\times 10^{-13}$	296	Cox *et al.*, 1984[1]	(a)
$(1.6^{+1.6}_{-0.8})\times 10^{-12}\exp[-(420 \pm 200)/T]$	278–338	Cox *et al.*, 1987[2]	(b)
Reviews and Evaluations			
4.0×10^{-13}	200–300	NASA, 1987[3]	(c)

Comments

(a) Time-dependent measurements of NO_3 in photolysis of Cl_2–$ClONO_2$–N_2 mixtures. ClO assumed to be produced in presence of excess NO_3 by reaction $Cl + NO_3$. $[NO_3]$ calculated using $\sigma = 1.7\times 10^{-17}$ cm^2 molecule^{-1} at 662 nm.

(b) Molecular modulation—UV absorption. Photolysis of Cl_2–$ClONO_2$–N_2 mixture. ClO monitored in UV at 277.2 nm ($\sigma = 7.2\times 10^{-18}$ cm^2) and NO_3 at 662 nm ($\sigma = 1.7\times 10^{-17}$ cm^2 molecule^{-1}). Rate constants obtained by computer modeling of absorption–time profiles for ClO in the presence of excess NO_3. Upper limit of $k_2/k_1 \leqslant 0.4$ based on absence of observable OClO.

(c) Based on Cox *et al.*[1,2] but no recommended temperature dependence.

Preferred Value

$k = 4.0\times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The two studies using a similar technique are in good agreement at 298 K. In view of the uncertainty in the data, the temperature dependence cannot be considered established and a temperature-dependent expression for k is not recommended from this evaluation. The weight of evidence presented[2] suggests that channel (1) is the major pathway at $T \leqslant 300$ K.

References

[1] R. A. Cox, R. A. Barton, E. Ljunstrom, and D. W. Stocker, Chem. Phys. Lett. **108**, 228 (1984).
[2] R. A. Cox, M. Fowles, D. Moulton, and R. P. Wayne, J. Phys. Chem. **91**, 3361 (1987).
[3] NASA Evaluation No. 8, 1987 (see References in Introduction).

$ClO + ClO \rightarrow Cl + ClOO$ (1)
$\rightarrow Cl + OClO$ (2)
$\rightarrow Cl_2 + O_2$ (3)

ΔH° (1) = 12 kJ mol^{-1}
ΔH° (2) = 18 kJ mol^{-1}
ΔH° (3) = -204 kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.8 \pm 1.7)\times 10^{-13}\exp[(-1250 \pm 150)/T]$	294–495	Clyne and Coxon, 1968[1]	(a)
9.1×10^{-15}	298		
$(6.5 \pm 1.0)\times 10^{-13}\exp[(-1150 \pm 50)/T]$	273–710	Clyne and White, 1971[2]	(b)
1.2×10^{-14}	298		
$(1.12 \pm 0.15)\times 10^{-14}$	298	Clyne, McKenney and Watson, 1975[3]	(c)
$(7.0 \pm 2.0)\times 10^{-15}$	298	Basco and Hunt, 1979[4]	(d)
$(9.1 \pm 2.0)\times 10^{-15}$	298	Cox and Derwent, 1979[5]	(e)
$(5.1^{+14.1}_{-3.7})\times 10^{-13}\exp[(-1350 \pm 400)/T]$	268–338	Hayman, Cox and Davis, 1986[6]	(f)
5.5×10^{-15}	298		
Reviews and Evaluations			
$1.53\times 10^{-12}\exp(-1238/T)$	273–710	Watson, 1977[7]	(g)
$8.0\times 10^{-13}\exp(-1250/T)$	200–300	NASA, 1987[8]	(h)

Comments

(a) Discharge flow–UV absorption detection of ClO at 277.2 nm. ClO produced from the reaction $Cl + OClO$. k values based on temperature-dependent values of σ_{ClO} given by $\sigma_{294\ K}/\sigma_T = 1 + 3.6\times10^{-3}\ (T-294)$ with $\sigma_{294} = 7.4\times10^{-18}$ cm^2 molecule^{-1} at 277.2 nm. 298 K value calculated from Arrhenius expression. Original definition of rate constant: $-d[ClO]/dt = k[ClO]^2$. Quoted values are a factor of 2 lower.

(b) Discharge flow–UV absorption detection of ClO at 277.2 nm using same σ as in note (a). No significant pressure dependence over range 0.4–8.0 Torr Ar + SF_6. 298 K value calculated from Arrhenius expression. Quoted k values are a factor of 2 lower than given in the paper.

(c) Discharge flow–MS detection of ClO. Calibration by titration using NO + ClO reaction and detection of NO_2^+. Cl atom products detected by resonance absorption; OClO product by mass spectrometry. No quantiative measurement of branching ratios but an estimated ratio $k_2/k = 0.043$ was obtained.

(d) Flash photolysis–UV absorption of ClO at 292 and 277.2 nm. Differential absorption in the 6-O and 11-O bands used but actual σ employed not stated. k obtained by extrapolation of data over range 50–600 Torr to zero pressure. Quoted value is a factor of 2 lower than given in paper due to definition of k.

(e) Modulated photolysis of Cl_2–O_3 mixtures. ClO and OClO by time-resolved differential absorption spectroscopy. Quantum yields for photosensitized decomposition of O_3 measured. k value is sum of values for individual channels that were $k_1 = (3.1\pm0.8)\times10^{-15}$, $k_2 = (1.5\pm0.4)\times10^{-15}$ and $k_3 = (4.5\pm1.0)\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K, obtained by computer simulation of experimental data. Pressure = 760 Torr.

(f) Molecular modulation–UV spectroscopy. ClO monitored by time-resolved absorption at 277.2 nm in photolysis of Cl_2–O_2 mixtures. k based on $\sigma = 7.26\times10^{-18}$ cm^2 molecule^{-1} at 298 K with temperature dependence given by Clyne and Coxon.[1] k obtained by linear extrapolation of pressure-dependent rate constants at $p < 25$ Torr to zero pressure. 298 K value calculated from the expression.

(g) Based on work of Clyne and Coxon,[1] Clyne and White,[2] and Clyne *et al.*[3]

(h) Based on the earlier work of Clyne and coworkers[1–3] as discussed by Watson.[7]

Preferred Values

$k = 1.0\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1/k = 0.34$; $k_2/k = 0.17$; $k_3/k = 0.49$ at 298 K.

Reliability

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

$\Delta(k_1/k) = \pm0.15$; $\Delta(k_2/k) = \pm0.1$; $\Delta(k_3/k) = \pm0.2$.

Comments on Preferred Values

Although the measurements of the overall rate coefficient for ClO decay obtained from discharge flow measurements using both UV absorption and MS detection of ClO are in good agreement, it is not possible to define the value of k for the bimolecular reaction or the branching ratio for the three channels with any certainty. The recent measurements of the pressure dependent component of the ClO + ClO reaction at low pressure (Hayman *et al.*[6]) indicate that some contribution of the reaction $ClO + ClO + M \Rightarrow Cl_2O_2 + M$ would have been present in the earlier low-pressure studies. Also the results of Cox and Derwent[5] show that the "molecular" channel, reaction (3), must be a major channel at 298 K and the recent data of Hayman *et al.*[6] indicate that k_3 has a significant activation energy. Thus, the earlier suggestion of Clyne and Watson[9] that the bimolecular channels of ClO + ClO reaction only produce radical products is probably incorrect. On the other hand, it is unclear to what extent the radical channels contribute to the overall bimolecular rate constant at zero pressure reported by Hayman *et al.*[6] The expression in the latter work gives $k_{298} = 5.5\times10^{-15}$ cm^3 molecule^{-1} s^{-1}, which is a factor of approximately 2 lower than the overall value from the earlier studies.

The preferred value for the overall rate coefficient at 298 K is a mean of the low-pressure value of Clyne *et al.*[3] and Cox and Derwent.[5] The branching ratios of 298 K accept the results of Cox and Derwent. No recommendation can be given for the temperature dependence of k for atmospheric conditions ($T\leqslant300$ K). For temperatures $\geqslant300$ K the temperature dependences of k_1 and k_2 can be derived on the basis of the 298 K values together with A factors A_1 and A_2 calculated from thermodynamic values of ΔS_1° and ΔS_2° (from Clyne and Watson[9]) and the rate constants of the reverse reactions $k_{-1} = 8.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (NASA) and $k_{-2} = 3.4\times10^{-11}\exp(160/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation). They are $k_1 = 6.1\times10^{-13}\exp(-1480/T)$ and $k_2 = 1.2\times10^{-12}\exp(-2040/T)$ cm^3 molecule^{-1} s^{-1}. k_3 probably has a positive temperature dependence,[6] but no recommendation can be made.

References

[1] M. A. A. Clyne and J. A. Coxon, Proc. Roy. Soc. London Ser. A **303**, 207 (1968).

[2] M. A. A. Clyne and I. F. White, Trans. Faraday Soc. **67**, 2068 (1971).

[3] M. A. A. Clyne, D. J. McKenney and R. T. Watson, J. Chem. Soc. Faraday 1 **71**, 322 (1975).

[4] N. Basco and J. E. Hunt, Int. J. Chem. Kinet. **11**, 649 (1979).

[5] R. A. Cox and R. G. Derwent, J. Chem. Soc. Faraday Trans 1 **75**, 1635 (1979).

[6] G. D. Hayman, J. M. Davies, and R. A. Cox, Geophys. Res. Lett. **13**, 1347 (1986).

[7] R. T. Watson, J. Phys. Chem. Ref. Data **6**, 871 (1977).

[8] NASA Evaluation No. 8, 1987 (see References in Introduction).

[9] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 **73**, 1169 (1977).

$ClO + ClO + M \rightarrow Cl_2O_2 + M$

$\mathfrak{S}\Delta H^\circ = -72.5$ kJ mol^{-1}

Low-pressure rate coefficients

k_o/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
5.0×10^{-32} [O_2]	298	Johnston, Morris and Van den Bogaerde, 1969[1]	(a)
3.3×10^{-32} [Ar]			
$(2.0\pm2.0)\times10^{-32}$ [Ar]	298	Walker, 1972[2]	(b)
1.1×10^{-32} [O_2]	300	Basco and Hunt, 1979[3]	(c)
3.5×10^{-33} [He]			
$(3.0\pm0.5)\times10^{-32}$[$N_2+O_2$]	298	Cox *et al.*, 1979[4]	(d)
$(6.0\pm0.4)\times10^{-32}(T/300)^{-(2.1\pm0.7)}$[$Cl_2+O_2$]	268–338	Hayman, Davies and Cox, 1986[5]	(e)
Reviews and Evaluations			
$4.0\times10^{-32}(T/300)^{-2.0}$ [air]	200–300	NASA, 1987[6]	(f)

Comments

(a) Molecular modulation–UV spectroscopy. Photolysis of Cl_2–O_2 mixtures; ClO monitored at 257.7 nm and k based on an absorption cross section of $\sigma = 4.83\times10^{-18}$ cm^2 molecule^{-1}.[7] Complex kinetic analysis used to derive k. Pressure range is 50–760 Torr.

(b) Discharge flow–UV absorption for ClO. Pressure range is 1–8 Torr.

(c) Flash photolysis of OClO and Cl_2–O_2 mixtures. ClO monitored by UV absorption spectroscopy at 292, 277.2, and 257.7 nm using values of 10^{18} σ (cm^2 molecule^{-1}) of 4.3, 7.6, and 5.0, respectively. Underlying absorption in the region 232–292 nm assigned to Cl_2O_2 which was equilibrated with ClO on long time scales. Pressure range 50–700 Torr. Quoted values are a factor of 2 lower than given in paper due to definition of k.

(d) Molecular Modulation–UV spectroscopy photolysis of Cl_2–O_2 mixtures. ClO monitored at 277.2 nm and k based on $\sigma_{277.2nm} = 7.26\times10^{-18}$ cm^2 molecule^{-1} (Clyne and Coxon). k based on measured steady state of ClO and not on complex kinetic decay. Pressure range is 40–300 Torr.

(e) Molecular Modulation with fully time-resolved detection of ClO kinetics in photolysis of Cl_2–O_2 mixtures. ClO monitored at 277.2 nm and k based on $\sigma = 7.26\times10^{-18}$ cm^2 molecule^{-1} at 277.2 nm and 298 K with temperature dependence of $\sigma_{294}/\sigma_T = 1 + 3.6\times10^{-3}$ (T–294) given by Clyne and Coxon. k obtained from data in the range 5–25 Torr with $M = Cl_2 + O_2$ in ratio 2:3.

(f) Recommendation based on all available experimental data in Refs. 1–5.

Preferred Values

$k_o = 4.0\times10^{-32}(T/300)^{-2.0}$ [N_2] cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability $\Delta \log k_o = \pm 0.2$ at 300 K.
$\Delta n = \pm 1.0$.

Comments on Preferred Values

Determination of the kinetics of this reaction is difficult because of (1) competing bimolecular channels that are dominant at low pressure and (2) the instability of the Cl_2O_2 product. Cox *et al.*[4] have proposed that the overall reaction can only be measured in the Cl_2–O_2 and other photolysis systems when sufficient Cl atoms are present to scavenge the Cl_2O_2 molecule and prevent its equilibration with ClO. Insufficient information was given in the flash photolysis study to assess the degree to which this complication may have affected the results. Nevertheless, the results of all studies are in reasonable agreement.

The value of Hayman *et al.*[5] is significantly higher than reported earlier, which may be due in part to a higher third body efficiency of Cl_2 relative to O_2 or N_2. In this study, falloff in k was observed at higher pressures but its mechanistic origin could not be distinguished. The preferred value is a mean of the values for $M = O_2$ from Johnston *et al.*,[2] Basco and Hunt,[3] and for $M = N_2 + O_2$ and $Cl_2 + O_2$ from Cox *et al.*[4] and Hayman *et al.*[5] The temperature dependence is based on that of Hayman *et al.*[5]

References

[1] H. S. Johnston, E. D. Morris, and J. Van den Bogaerde, J. Amer. Chem. Soc. **91**, 7712 (1969).

[2] R. W. Walker, Ph. D. thesis, Queen Mary College, University of London, 1972.

[3] N. Basco and J. K. Hunt, Int. J. Chem. Kinet. **11**, 649 (1979).

[4] R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and H. J. Reid, J. Chem. Soc. Faraday 1 **75**, 1648 (1979).

[5] G. D. Hayman, J. M. Davies, and R. A. Cox, Geophys. Res. Lett. **13**, 1347 (1986).

[6] NASA Evaluation No. 8, 1987 (see References in Introduction).

[7] M. A. A. Clyne and J. A. Coxon, Proc. Roy. Soc. London Ser. A **303**, 207 (1968).

$Cl_2O_2+M \rightarrow ClO+ClO+M$

ⓢ$\Delta H^\circ = 72.5$ kJ mol^{-1}

Low-pressure rate coefficients

k/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.5 \pm 2.3)\times10^{-18}$ [O_2]	298	Cox and Derwent, 1979[1]	(a)
Relative Rate Coefficient			
2.1×10^{-18} [O_2]	298	Basco and Hunt, 1979[2]	(b)
$3.1\times10^{-5}(T/300)^{-3}\exp(-8720/T)$ [N_2]	233–300	Cox and Hayman, 1988[3]	(c)

Comments

(a) Modulate photolysis of Cl_2–O_3–O_2 mixtures. ClO measured by differential UV absorption at 277 nm using $\sigma = 7.26\times10^{-18}$ cm^2 molecule^{-1} (Ref. 4) as a standard for calibrating [ClO]. k obtained by modeling complex kinetic decay of ClO.

(b) k obtained from ratio of k/k^* for the ClO + ClO + M reaction, where $k = 1.1\times10^{-32}$ cm^6 molecule^{-2} s^{-1} ($M = O_2$) and $K = (5.2 \pm 0.2)\times10^{-15}$ cm^3 molecule^{-1} at 298 K determined in the same study using flash photolysis–UV absorption technique.

(c) K for the ClO + ClO + M$\Leftrightarrow$$Cl_2O_2$ + M reaction determined from measurements of ClO and Cl_2O_2 in equilibrium in steady-state photolysis of Cl_2–Cl_2O–N_2 mixtures. k calculated using the value of k(ClO + ClO + M) from this evaluation. $K = (4.2 \pm 0.3)\times10^{-30}T\exp[(8720 \pm 360)/T]$ cm^3 molecule^{-1}. Pressure = 1 atm (N_2).

Preferred Values

$k_0 = 6\times10^{-18}$ [N_2]s^{-1} at 298 K.
$k_0 = 3.1\times10^{-5}(T/300)^{-3}\exp(-8720/T)$ [N_2]s^{-1} over range 230–300 K.

Reliability

$\Delta \log k = \pm 0.5$ at 300 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred value is based on the recent measurements of Cox and Hayman[3] which are in reasonable agreement with both the earlier measurements at 298 K. More work of a direct nature on the decomposition of Cl_2O_2 at low temperatures is required

References

[1] R. A. Cox and R. G. Derwent, J. Chem. Soc. Faraday 1 **75**, 1635 (1979).
[2] N. Basco and J. E. Hunt, Int. J. Chem. Kinet. **11**, 649 (1979).
[3] R. A. Cox and G. D. Hayman, Nature **322**, 796 (1988).
[4] M. A. A. Clyne and J. A. Coxon, Proc. Roy. Soc. London **A303**, 207 (1968).

$OClO+NO \rightarrow NO_2+ClO$

$\Delta H^\circ = -56$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.4 \pm 0.5)\times10^{-13}$	298	Bemand, Clyne, and Watson, 1973[1]	(a)
Reviews and Evaluations			
3.4×10^{-13}	298	Watson, 1977[2]	(b)
$2.5\times10^{-12}\exp(-600/T)$	200–300	NASA, 1987[3]	(c)

Comments

(a) Discharge flow–mass spectrometric determination of OClO decay in the presence of excess NO. Secondary reactions as a result of Cl generation from ClO + NO $\Rightarrow$ NO_2 + Cl suppressed by addition of NOCl or Br_2.

(b) Accepts results of Bemand *et al.*[1]

(c) Arrhenius parameters estimated using 298 K value of Bemand *et al.*[1]

Preferred Value

$k = 3.4\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is based on the only direct study of this reaction reported by Bemand *et al.*[1] In the absence of experimental data no recommendation is given for the temperature dependence.

References

[1] B. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 **69**, 1356 (1973).
[2] R. T. Watson, J. Phys. Chem. Ref. Data **6**, 871 (1977).
[3] NASA Evaluation No. 8, 1987 (see References in Introduction).

$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$

$\Delta H^\circ = -211$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$< 1.7 \times 10^{-19}$	298	Rowland *et al.*, 1986[1]	(a)
$< 2.0 \times 10^{-21}$	298	Atkinson *et al.*, 1986[2]	(b)
$< 3.4 \times 10^{-21}$	296	Hatakeyama and Leu, 1986[3]	(c)
Reviews and Evaluations			
$< 2 \times 10^{-21}$	200–300	NASA, 1987[4]	*

Comments

(a) IR absorption spectroscopy of $ClONO_2$–H_2O mixtures in coated Pyrex cell. Heterogeneous reaction more or less independent of surface type.

(b) FTIR spectroscopic measurements in large environmental chambers—Teflon coated. $ClONO_2$ decay in excess H_2O (3–440×10^{15} molecule cm^{-3}). Rate constant is chamber dependent, indicating heterogeneous reaction. Gaseous HNO_3 and HOCl produced but yields in range 0.65–0.85.

(c) FTIR spectroscopy in static Pyrex cell. First-order kinetic decay of $ClONO_2$ in presence of excess H_2O (up to 1×10^{17} molecule cm^{-3}). Observed reaction probably part heterogeneous. HNO_3 yield only 0.85.

Preferred Value

$k < 5.0 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

The upper limit is a conservative value based on the experiments of Hatakeyama and Leu.[3] Rossi *et al.*[5] have studied the heterogeneous reaction between $ClONO_2$ and H_2O in Knudsen Cell coupled to a MS. Accommodation coefficient γ for efficiency of removal of $ClONO_2$ at an H_2SO_4–H_2O liquid surface. γ was 3.2×10^{-4}, comparison with results in chambers indicates strong catalysis of the surface reaction by H_2SO_4.

References

[1] F. S. Rowland, H. Sato, H. Khwaja, and S. M. Elliott, J. Phys. Chem. **90**, 1985 (1986).
[2] R. Atkinson, E. C. Tuazon, H. MacLeod, S. M. Aschmann, and A. M. Winer, Geophys. Res. Lett. **31**(1), 117 (1986).
[3] S. Hatakeyama and M. T. Leu, Geophys. Res. Lett. **13**, 1343 (1986).
[4] NASA Evaluation No. 8, 1987 (see References in Introduction).
[5] M. J. Rossi, R. Malhotra, and D. M. Golden, Geophys. Res. Lett. **14**, 127 (1987).

$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$

$\Delta H^\circ = -69.2$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$< 1.2 \times 10^{-15}$	298	Birks *et al.*, 1977[1]	(a)
$< 1.0 \times 10^{-19}$	230–295	Molina *et al.*, 1986[2]	(b)
$< 1.5 \times 10^{-19}$	298	Atkinson *et al.*, 1987[3]	(c)
$< 5.0 \times 10^{-18}$	296	Friedl, Goble, and Sander, 1986[4]	(d)
$< 8.4 \times 10^{-21}$	296	Hatakeyama and Leu, 1986[5]	(e)
Reviews and Evaluations			
$< 1.0 \times 10^{-18}$	200–300	NASA, 1985[6]	(f)
$< 1.0 \times 10^{-20}$	200–300	NASA, 1987[7]	(g)

Comments

(a) DF–MS; reduction of $ClONO_2$ in presence of HCl; Cl_2 produced. Rate was surface dependent, indicating heterogeneous reaction.

(b) FTIR detection of reactants and HNO_3, UV detection of Cl_2. Static and flow reactors used. Rapid reaction on vessel walls but no reaction in gas phase. Very little temperature dependence of rate over range 230–295 K.

(c) FTIR spectroscopy in large environmental chambers—Teflon surfaces. Reaction gives HNO_3 with a yield of 1.0 ± 0.05. Rate depends on surface, degree of mixing and shows nonlinear dependence on reactant concentrations. k is upper limit value for homogeneous reaction.

(d) Flow reactor–FTIR spectrospcopy. Heterogeneous reaction observed with complex dependence of rate on total pressure, [HCl], etc., k is upper limit value for homogeneous reaction.

(e) Static reactor–FTIR spectroscopy; heterogeneous reaction; rate described in terms of Langmuir absorption isotherm for HCl. Upper limit value of k for homogeneous reaction based on data at high [HCl] where heterogeneous component is saturated.

(f) Based on work of Molina *et al.*[2]

(g) Based on Hatakeyama and Leu.[5]

Preferred Value

$k < 2.0 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

All studies are consistent with a very slow rate for the gas-phase reaction between the HCl and chlorine nitrate. The preferred value at 298 K is based on the slowest observed values (Hatakeyama and Leu[5]). The work of Molina *et al.*[2] shows that this is probably applicable at stratospheric temperatures as well. Recent work of Molina *et al.*[8] and Tolbert *et al.*[9] shows that the heterogeneous reaction is probably important in the stratosphere.

References

[1] J. W. Birks, B. Shoemaker, T. J. Leck, R. A. Borders, and L. J. Hart, J. Chem. Phys. **66**, 5491 (1977).

[2] L. T. Molina, M. J. Molina, R. A. Stachnik, and R. D. Tom, J. Phys. Chem. **89**, 3779 (1985).

[3] R. Atkinson, S. M. Aschmann, E. C. Tuazon, M. A. Goodman, and A. M. Winer, J. Atmos. Chem. **5**, 83 (1987).

[4] R. R. Friedl, J. H. Goble, and S. P. Sander, Geophys. Res. Lett. **13**, 1351 (1986).

[5] S. Hatakeyama and M.-T. Leu, Geophys. Res. Lett. **13**, 1343 (1986).

[6] NASA Evaluation No. 7, 1985 (see References in Introduction).

[7] NASA Evalaution No. 8, 1987 (see References in Introduction).

[8] M. J. Molina, T. L. Tso, L. T. Molina, and F. C.-Y. Wang, Science **238**, 1253 (1987).

[9] M. A. Tolbert, M. J. Rossi, R. Malhotra, and D. M. Golden, Science **238**, 1258 (1987).

$CF_3 + O_2 + M \rightarrow CF_3O_2 + M$

$\Delta H^\circ = -141$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.8 \pm 0.4) \times 10^{-29}$[He]	298	Ryan and Plumb, 1982[1]	(a)
$(4.5 \pm 1.0) \times 10^{-29}[N_2]$	298	Caralp and Lesclaux, 1983[2]	(b)
$(1.9 \pm 0.2) \times 10^{-29}(T/300)^{-4.7 \pm 0.4}[N_2]$	233–373	Caralp, Lesclaux, and Dognon, 1986[3]	(c)
$(1.6 \pm 0.2) \times 10^{-29}$[He]	298		
Reviews and Evaluations			
$1.5 \times 10^{-29}(T/300)^{-4}$[air]	200–300	NASA, 1987[4]	(d)

Comments

(a) Microwave discharge–flow system coupled to a quadrupole mass spectrometer. CF_3 decay monitored under pseudo-first-order conditions. Falloff curve measured over the range 0.5–8.3 Torr. Extrapolation to the low- and high-pressure limits using F_c in the range 0.35–0.42. k_0 relatively insensitive to F_c.

(b) Pulsed laser photolysis–mass spectrometry. Pressure range 0.2–12 Torr. k_0 from falloff extrapolation using $F_c = 0.6$. k_0 relatively insensitive to F_c.

(c) As (b). Temperature dependence of F_c represented as $F_c = \exp(-T/395)$.

(d) Based on Ref. 3.

Preferred Values

$k_0 = 1.9 \times 10^{-29}(T/300)^{-4.7}[N_2]$ cm^3 molecule^{-1} s^{-1} over the range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

Good agreement between Refs. 1 and 3 at 298 K for M = He. Preferred valued from Ref. 3. ΔH° estimated in Ref. 3.

High-pressure rate coefficients
Rate coefficients data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.0 \pm 0.03) \times 10^{-11}$	298	Cooper *et al.*, 1980[5]	(a)
$(8.0 \pm 1) \times 10^{-12}$	295	Ryan and Plumb, 1982[1]	(b)
$(9.0 \pm 2) \times 10^{-12}$	233–373	Caralp, Lesclaux, and Dognon, 1986[3]	(c)
Reviews and Evaluations			
$8.5 \times 10^{-12}/T/300)^{-1}$	200–300	NASA, 1987[4]	(d)

Comments

(a) Pulse radiolysis of CF_3Cl. CF_3O_2 detected by UV absorption spectroscopy. Measurements at 700 Torr of Ar.

(b) See comment (a) for k_0. k_∞ extrapolated using $F_c = 0.38$. Results are sensitive to F_c.

(c) See comment (b) for k_0. Results are sensitive to F_c.

(d) Average of results from Refs. 1 and 3. T-dependence estimated.

Preferred Values

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

Reliability

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

Comments on Preferred Values

The available measurements all agree fairly well. The k_∞ value from Ref. 5 is preferred since it is the only direct high-pressure measurement and nearly independent of uncertainties in F_c.

Intermediate Falloff Range

For the given k_0 and k_∞ values, the measurements are consistent with $F_c = 0.4$–0.5.

References

[1] K. R. Ryan and I. C. Plumb, J. Phys. Chem. **86**, 4678 (1982).
[2] F. Caralp and R. Lesclaux, Chem. Phys. Lett. **102**, 54 (1983).
[3] F. Caralp, R. Lesclaux, and A. M. Dognon, Chem. Phys. Lett. **129**, 433 (1986).
[4] NASA Evaluation No. 8, 1987 (see References in Introduction).
[5] R. Cooper, J. B. Cumming, S. Gordon, and W. A. Mulac, Rad. Phys. Chem. **16**, 169 (1980).

$CFCl_2 + O_2 + M \rightarrow CFCl_2O_2 + M$

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.0 \pm 0.8) \times 10^{-30}[N_2]$	298	Caralp and Lesclaux, 1983[1]	(a)
Reviews and Evaluations			
$5.0 \times 10^{-30}(T/300)^{-2}[\text{air}]$	200–300	NASA, 1987[2]	(b)

Comments

(a) Pulsed laser photolysis–mass spectroscopy. Falloff curve measured over the range 0.2–12 Torr, extrapolated to k_0 using $F_c = 0.6$.

(b) Based on Ref. 1, T-dependence estimated.

Preferred Values

$k_0 = 5 \times 10^{-30}(T/300)^{-4}[N_2]$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

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

$\Delta n = \pm 2$.

Comments on Preferred Values

Since there is only a single measurement, large error limits are assigned. The T-dependence is taken close to the measurement on $CF_3 + O_3 + M$ (see this evaluation).

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.0 \pm 1) \times 10^{-12}$	298	Caralp and Lesclaux, 1983[1]	(a)
Reviews and Evaluations			
$6 \times 10^{-12}(T/300)^{-1}$	200–300	NASA, 1987[2]	(b)

Comments

(a) See comment (a) for k_0. Extrapolation of the falloff curve using $F_c = 0.6$. The k_∞ value derived is fairly uncertain.

(b) Based on Ref. 1. T-dependence estimated.

Preferred Values

$k_\infty = 6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

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

Comments on Preferred Values

The value of k_∞ remains relatively uncertain until high-pressure measurements are made and/or F_c is known more precisely. The T-dependence is taken as for $CF_3 + O_2 + M$ (see this evaluation).

Intermediate Falloff Range

The given k_0- and k_∞- values were derived using an estimated $F_c = 0.6$.

References

[1] F. Caralp and R. Lesclaux, Chem. Phys. Lett. **102**, 54 (1983).
[2] NASA Evaluation No. 7, 1987 (see References in Introduction).

$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.8 \pm 0.6) \times 10^{-31}$[He]	295	Ryan and Plumb, 1984[1]	(a)
Reviews and Evaluations			
$1.0 \times 10^{-30}(T/300)^{-2}[N_2]$	200–300	NASA, 1987[2]	(b)

Comments

(a) Microwave discharge–flow system using quadrupole mass spectrometry. CCl_3 generated by the reaction $F + CHCl_3 \rightarrow CCl_3 + HF$. Falloff curve studied over the pressure range 1.7–5.4 Torr, k_0 obtained using $F_c = 0.25$.

(b) Based on data from Ref. 1. Using a falloff representation with $F_c = 0.6$ and assuming $k_0(M = He):k_0(M = N_2) = 1:2.5$. T-dependence estimated.

Preferred Values

$k_0 = 1.5 \times 10^{-30}(T/300)^{-4}[N_2]$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

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

$\Delta n = \pm 2$.

Comments on Preferred Values

The preferred value accepts $F_c = 0.25$ and $k_0(M = N_2):k_0(M = He) = 2.5:1$. The T-dependence is estimated close to the measurements on $CF_3 + O_2 + M$ (see this evaluation).

High-pressure coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.1 \pm 0.5) \times 10^{-12}$	300	Cooper *et al.*, 1980[3]	(a)
2.5×10^{-12}	295	Ryan and Plumb, 1984[1]	(b)
Reviews and Evaluations			
$2.5 \times 10^{-12}(T/300)^{-1}$	200–300	NASA, 1987[2]	(c)

Comments

(a) CF_3 generated by pulse radiolysis of CCl_4 at 700 Torr of He. CCl_3O_2 detected by UV absorption spectroscopy.

(b) See comment (a) for k_0.

(c) Based on Ref. 1, T-dependence estimated.

Preferred Values

$k_\infty = 5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} 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 value is based on the sole high-pressure measurement of Ref. 3. The T-dependence is estimated by analogy to the $CF_3 + O_2 + M$ reaction (see this evaluation).

Intermediate Falloff Range

The available falloff data from Ref. 1 are consistent with the preferred k_0- and k_∞-values using $F_c = 0.25$.

References

[1] K. R. Ryan and I. C. Plumb, Int. J. Chem. Kinet. **16**, 591 (1984).

[2] NASA Evaluation No. 8, 1987 (see References in Introduction).

[3] R. Cooper, J. B. Cumming, and W. A. Mulac, Rad. Phys. Chem. **16**, 169 (1980).

$CClX_2O \rightarrow CX_2O + Cl$

(X = F or Cl)

Comment

The $CClX_2O$ radicals are relatively unstable, decomposing rapidly at room temperature to give Cl together with the corresponding carbonyl compound. Information on the rates of the thermal elimination of a Cl atom from the $CClX_2O$ radical comes mainly from studies of the photooxidation of CHX_3-type compounds. Long reaction chains have been characterized in the direct photolysis or Cl_2 photosensitized oxidation of $CHCl_3$, $CHFCl_2$, and CHF_2Cl,[1–3] the release of a Cl atom in the above reaction being the main chain carrier. Carr[4] obtained $k(CF_2ClO \rightarrow CF_2O + Cl) = 7 \times 10^5$ s^{-1} at room temperature in their complex analysis of the results for flash photolysis of 1,3 dichlorotetrafluoroacetone in the presence of O_2. Lesclaux and coworkers have obtained

$k(CCl_3O \rightarrow CCl_2O + Cl) > 1 \times 10^5$ s^{-1} at 233 K and 7.5 Torr pressure.

$k(CCl_2FO \rightarrow CClFO + Cl) > 3 \times 10^4$ s^{-1} at 253 K and 6.7 Torr pressure.

Thus these reactions are expected to occur rapidly even at stratospheric temperatures and competing pathways need not be considered in the atmospheric oxidation of chlorofluoromethanes.

References

[1] E. Sanhueza, J. Photochem. **7**, 325 (1977).

[2] S. Hautecloque, J. Photochem. **14**, 157 (1980).

[3] R. Lesclaux, A. M. Dognon, and F. Caralp, J. Photochem. Soc. A **41**, 1 (1987).

[4] R. W. Carr, D. G. Peterson, and F. K. Smith, J. Phys. Chem. **90**, 607 (1986).

$RO_2 + NO \rightarrow RO + NO_2$

($R = CF_3, CF_2Cl, CFCl_2, CCl_3$)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$R = CF_3$			
$(1.78 \pm 0.36) \times 10^{-11}$	295	Plumb and Ryan, 1982[1]	(a)
$(1.45 \pm 0.2) \times 10^{-11} (T/298)^{-(1.2 \pm 0.2)}$	230–430	Dognon, Caralp, and Lesclaux, 1985[2]	(b)
$(1.45 \pm 0.2) \times 10^{-11}$	298		
$R = CF_2Cl$			
$(1.6 \pm 0.3) \times 10^{-11} (T/298)^{-(1.5 \pm 0.4)}$	230–430	Dognon, Caralp, and Lesclaux, 1985[2]	(b)
$(1.6 \pm 0.3) \times 10^{-11}$	298		
$R = CFCl_2$			
$(1.6 \pm 0.2) \times 10^{-11}$	298	Lesclaux and Caralp, 1984[3]	(c)
$(1.45 \pm 0.2) \times 10^{-11} (T/298)^{-(1.3 \pm 0.2)}$	230–430	Dognon, Caralp, and Lesclaux, 1985[2]	(b)
$(1.45 \pm 0.2) \times 10^{-11}$	298		
$R = CCl_3$			
$(1.86 \pm 0.28) \times 10^{-11}$	295	Ryan and Plumb, 1984[4]	(d)
$(1.7 \pm 0.2) \times 10^{-11} (T/298)^{-(1.0 \pm 0.2)}$	230–430	Dognon, Caralp, and Lesclaux, 1985[2]	(b)
$(1.7 \pm 0.2) \times 10^{-11}$	298		
Reviews and Evaluations			
$R = CF_3$			
$3.9 \times 10^{-12} \exp[(400 \pm 200)/T]$	230–430	NASA, 1985[5]	(e)
$3.9 \times 10^{-12} \exp[(400 \pm 200)/T]$	230–430	NASA, 1987[6]	(e)
$R = CF_2Cl$			
$3.1 \times 10^{-12} \exp[(500 \pm 200)/T]$	230–430	NASA, 1985[5]	(e)
$3.1 \times 10^{-12} \exp[(500 \pm 200)/T]$	230–430	NASA, 1987[6]	(e)
$R = CFCl_2$			
$3.5 \times 10^{-12} \exp[(430 \pm 200)/T]$	230–430	NASA, 1985[5]	(e)
$3.5 \times 10^{-12} \exp[(430 \pm 200)/T]$	230–430	NASA, 1987[6]	(e)
$R = CCl_3$			
$5.7 \times 10^{-12} \exp[(330 \pm 200)/T]$	230–430	NASA, 1985[5]	(e)
$5.7 \times 10^{-12} \exp[(330 \pm 200)/T]$	230–430	NASA, 1987[6]	(e)

Comments

(a) Discharge flow–mass spectrometry. Value of k independent of pressure in the range 1.9–5.1 Torr.

(b) Pulsed laser photolysis–mass spectrometry. No significant pressure dependence of k in the range 1–10 Torr.

(c) Pulsed laser photolysis–mass spectrometry. Measurement made at 2 Torr total pressure.

(d) Discharge flow–mass spectrometry. Value of k independent of pressure in the range 1.7–5.4 Torr.

(e) Recommendation based on the results of Dognon *et al.*[2]

Preferred Values

$R = CF_3$

$k = 1.6 \times 10^{-11} (T/300)^{-1.2}$ cm^3 molecule^{-1} s^{-1} over range 230–430 K.

$\Delta \log k = \pm 0.2$ over range 230–430 K.

$R = CF_2Cl$

$k = 1.6 \times 10^{-11} (T/300)^{-1.5}$ cm^3 molecule^{-1} s^{-1} over range 230–430 K.

$\Delta \log k = \pm 0.3$ over range 230–430 K.

$R = CFCl_2$

$k = 1.45 \times 10^{-11} (T/300)^{-1.3}$ cm^3 molecule^{-1} s^{-1} over range 230–430 K.

$\Delta \log k = \pm 0.2$ over range 230–430 K.

$R = CCl_3$

$k = 1.8 \times 10^{-11} (T/300)^{-1.0}$ cm^3 molecule^{-1} s^{-1} over range 230–430 K.

$\Delta \log k = \pm 0.2$ over range 230–430 K.

Comments on Preferred Values

$R = CF_3$

The preferred values are based on the temperature-dependent data of Dognon *et al.*[2] and the 298 K value of Plumb and Ryan.[1]

$R = CF_2Cl$

The preferred values are given by the expression of Dognon *et al.*[2]

$R = CFCl_2$

The preferred values are based on the temperature-dependent data of Dognon *et al.*[2] These data supersede the previous result of Lesclaux and Caralp.[3]

$R = CCl_3$

The preferred values are based on the temperature-dependent data of Dognon *et al.*[2] and the 298 K value of Ryan and Plumb.[4]

The temperature dependence expressions are given in the form favored by Dognon *et al.*,[2] which best describe the measured data. If Arrhenius expression are required, then the expressions recommended in NASA 1987[6] should be employed. In view of the consistent observation of pressure independence, it seem unlikely that $RONO_2$ is produced as a product. Dognon *et al.*[2] measured quantum yields for NO_2 greater than unity for all the RO_2 radicals suggesting that the $RO_2 + NO$ reaction form RO and NO_2 exclusively, with additional NO_2 produced from secondary chemistry.

References

[1] I. C. Plumb and K. R. Ryan, Chem. Phys. Lett. **92**, 236 (1982).
[2] A. M. Dognon, F. Caralp and R. Lesclaux, J. Chim. Phys. **82**, 349 (1985).
[3] R. Lesclaux and F. Caralp, Int. J. Chem. Kinet. **16**, 1117 (1984).
[4] K. R. Ryan and I. C. Plumb, Int. J. Chem. Kinet. **16**, 591 (1984).
[5] NASA Evaluation No. 7, 1985 (see References in Introduction).
[6] NASA Evaluation No. 8, 1987 (see References in Introduction).

$CF_3O_2 + NO_2 + M \rightarrow CF_3O_2NO_2 + M$

$\Delta H° \approx -105$ kJ mol^{-1}

Low-pressure rate coefficents
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.7 \pm 0.8) \times 10^{-29}(T/298)^{-4.7\pm1}[O_2]$	233–373	Caralp *et al.*, 1988[1]	(a)

Comments

(a) Pulsed laser photolysis and time-resolved mass spectrometry. Falloff curve measured over the pressure range 1–10 Torr. Falloff extrapolation using $F_c = \exp(-T/416)$. Increasing width of falloff curve included via N from Ref. 2.

Preferred Values

$k_0 = 2.7 \times 10^{-29}(T/300)^{-5}[N_2]$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

The falloff extrapolation of the only data from Ref. 1 to k_0 appears relatively insensitive to uncertainties in F_c. $\Delta H°$ was estimated in Ref. 1.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.9 \times 10^{-12}(T/300)^{-0.72\pm0.3}$	233–373	Caralp *et al.*, 1988[1]	(a)

Comments

(a) See comment for k_0.

Preferred Values

$k_\infty = 9 \times 10^{-12}(T/300)^{-0.7}$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The extrapolation of the falloff curve of the only data from Ref. 1 to k_∞ appears less certain than that to k_0.

Intermediate Falloff Range

The given k_0- and k_∞- values are consistent with the measurements if $F_c = \exp(-T/416)$ is used. This corresponds to $F_c(300\ \text{K}) = 0.49$.

References

[1] F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2 **84**, 569 (1988).
[2] J. Troe, J. Phys. Chem. **83**, 114 (1979).

$CF_2ClO_2 + NO_2 + M \rightarrow CF_2ClO_2NO_2 + M$

$\Delta H^\circ \approx -105$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.0 \pm 2.0) \times 10^{-29} (T/298)^{-5.1 \pm 1} [O_2]$	233–373	Caralp *et al.*, 1988[1]	(a)

Comments

(a) Pulsed laser photolysis and time-resolved mass spectrometry. Falloff curve measured over the pressure range 1–10 Torr. Falloff extrapolation using $F_c = \exp(-T/373)$. Increasing width of falloff curve included via N from Ref. 2.

Preferred Values

$k_0 = 4.0 \times 10^{-29} (T/300)^{-5} [N_2]$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.4$ at 300 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

The preferred values are based on the only available data from Ref. 1. ΔH° was estimated in Ref. 1.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.0 \times 10^{-11} (T/298)^{-0.66 \pm 0.3}$	233–373	Caralp *et al.*, 1988[1]	(a)

Comments

(a) See comment for k_0.

Preferred Values

$k_\infty = 1.0 \times 10^{-11} (T/300)^{-0.7}$ over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the only available data from Ref. 1.

Intermediate Falloff Range

The extrapolated k_0- and k_∞- values were obtained using $F_c = \exp(-T/373)$ corresponding to $F_c(300\text{ K}) = 0.45$.

References

[1] F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2 **84**, 569 (1988).
[2] J. Troe, J. Phys. Chem. **83**, 114 (1979).

$CF_2ClO_2NO_2 + M \rightarrow CF_2ClO_2 + NO_2 + M$

Low-pressure rate coefficient
Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.24 \times 10^{-3} \exp(-10\,520/T) [N_2]$	265–288	Zabel, 1987[1]	(a)
$5.8 \times 10^{-19} [N_2]$	298*		

Comments

(a) *In situ* production of $CF_2ClO_2NO_2$ by UV photolysis of Cl_2–CHF_2Cl–NO_2–O_2–N_2 mixtures. Time dependence of $CF_2ClO_2NO_2$ monitored by long path FTIR. Decomposition measured upon addition of large excess of NO to scavenge CF_2ClO_2. Pressure range 8–600 Torr. Falloff extrapolation using $F_c = 0.40$; increasing width of falloff curve accounted for by using N from Ref. 2.

Preferred Values

$k_0 = 5.6\times10^{-4}\ \exp(-9310/T)[N_2]\ s^{-1}$ over the range 260–290 K.

$k_0 = 1.5\times10^{-17}[N_2]\ s^{-1}$ at 298 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are based on the experiments from Ref. 1, which appear consistent[1] with theoretical models, leading to collision efficiencies of $\beta_c = 0.35$. A relative efficiency $k_0(O_2){:}k_0(N_2) = 0.8$ was also derived in Ref. 1.

High-pressure rate coefficients
Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.0\times10^{16}\exp(-11\,880/T)$	265–288	Zabel, 1987[1]	(a)
4.9×10^{-2}	298*		

Comments

(a) See comment for k_0.

Preferred Values

$k_\infty = 1.0\times10^{16}\exp(-11\,880/T)\ s^{-1}$ over the range 260–290 K.

$k_\infty = 4.9\times10^{-2}\ s^{-1}$ at 298 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are based on the data from Ref. 1.

Intermediate Falloff Range

The extrapolated k_0 and k_∞ values were obtained using $F_c = 0.4$ in close agreement with the corresponding $F_c = \exp(-T/373)$ of the reverse reaction.[3]

References

[1] F. Zabel, in Proceedings of the International Conference on Photochemistry, Budapest, August 1987 (to be published).

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

[3] F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2 **84**, 569 (1988).

$CFCl_2O_2 + NO_2 + M \rightarrow CFCl_2O_2NO_2 + M$

$\Delta H^\circ \approx -105\ kJ\ mol^{-1}$

Low-pressure rate coefficients
Rate coefficient data

$k_0/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5\pm0.5)\times10^{-29}[O_2]$	298	Lesclaux and Caralp, 1984[1]	(a,b)
$(3.5\pm0.5)\times10^{-29}/T/298)^{-4.1}[O_2]$	233–373	Lesclaux, Caralp, and Dognon, 1986[2]	(a,b)
$(5.5\pm1.6)\times10^{-29}(T/298)^{-5.5\pm1.2}[O_2]$	233–373	Caralp *et al.*, 1988[3]	(a,c)
Reviews and Evaluations			
$3.5\times10^{-29}(T/300)^{-4}[air]$	200–300	NASA, 1988[4]	(d)

Comments

(a) Pulsed laser photolysis–mass spectrometry. Measurements over the pressure range 1–10 Torr.

(b) Falloff extrapolation using $F_c = 0.6$.

(c) Falloff extrapolation using $F_c = \exp(-T/342)$. Increasing width of falloff curve included via N from Ref. 5.

(d) Based on data from Ref. 2, using estimated T dependence.

Preferred Values

$k_0 = 5.5\times10^{-29}(T/300)^{-5}[N_2]$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The experimental results from Refs. 1–3 agree fairly well. Part of the differences in the derived k_0 values are due to different F_c-values employed. ΔH° estimated in Ref. 3.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.0 \pm 1.0)\times10^{-12}$	298	Lesclaux and Caralp, 1984[1]	(a,b)
$(5.9 \pm 1.0)\times10^{-12}(T/298)^{-0.72\pm0.3}$	233–373	Lesclaux, Caralp, and Dognon, 1986[2]	(a,b)
$8.3 \pm 10^{-12}(T/298)^{-0.66\pm0.3}$	233–373	Caralp *et al.*, 1988[3]	(a,c)
Reviews and Evaluations			
$6\times10^{-12}(T/300)^{-2}$	200–300	NASA, 1987[4]	(d)

Comments

(a), (b), and (c). See comments for k_0.

(d) Based on data from Ref. 2. T dependence estimated.

Preferred Values

$k_\infty = 8.3\times10^{-12}(T/300)^{-0.7}$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The experimental results from Refs. 1–3 agree fairly well. For molecules of this size, F_c different from the NASA standard value $F_c = 0.6$ have to be employed.

Intermediate Falloff Range

The derived k_0 and k_∞ values were obtained using $F_c = \exp(-T/342)$ corresponding to $F_c(300\text{ K}) = 0.42$.

References

[1] R. Lesclaux and F. Caralp, Int. J. Chem. Kinet. **16**, 1117 (1984).

[2] R. Lesclaux, F. Caralp, and A. M. Dognon, Geophys. Res. Lett. **13**, 933 (1986).

[3] F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2 **84**, 569 (1988).

[4] NASA Evaluation No. 8, 1987 (see References in Introduction).

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

$CFCl_2O_2NO_2 + M \rightarrow CFCl_2O_2 + NO_2 + M$

Low-pressure rate coefficients
Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.0\times10^{-3}\exp(-10\,570/T)[N_2]$	273–290	Zabel, 1987[1]	(a)
$1.2\times10^{-18}[N_2]$	298*		

Comments

(a) *In situ* production of $CFCl_2O_2$ by UV photolysis of Cl_2–$CHFCl_2$–NO_2–O_2–N_2 mixtures. Time dependence of $CFCl_2O_2NO_2$ monitored by long path FTIR. Decomposition measured upon addition of large excess of NO to scavenge $CFCl_2O_2$. Pressure range 8–600 Torr. Falloff extrapolation using $F_c = 0.40$; increasing width of falloff curve accounted for by using N from Ref. 2.

Preferred Values

$k_0 = 3\times10^{-3}\exp(-10\,570/T)[N_2]$ s^{-1} over the range 270–290 K.

$k_0 = 1.2\times10^{-18}[N_2]$ s^{-1} at 298 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are based on the experiments from Ref. 1, which appear consistent[1] with theoretical models, leading to collision efficiencies of $\beta_c = 0.21$.

High-pressure rate coefficients
Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.0\times10^{16}\exp(-12\,300/T)$	274–305	Simonaitis, Glavas, and Heicklen, 1979[3]	(a)
0.047	298		
$2.1\times10^{16}\exp(-11\,980/T)$	273–290	Zabel, 1987[1]	(b)
0.073	298*		

Comments

(a) Steady-state photolysis of Cl_2–$CHFCl_2$–O_2–N_2–NO–NO_2 mixtures at 1 atm. Simulation of the mechanism dependent on various Cl-consuming reactions k assumed to be close to k_∞.

Preferred Values

$k_\infty = 2.1\times10^{16}\exp(-11\,980/T)$ s^{-1} over the range 270–290 K.

$k_\infty = 7.3\times10^{-2}$ s^{-1} at 298 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$.

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

Comments on Preferred Values

Since the experiments of Ref. 1 provide a more direct access to the decay of $CFCl_2O_2NO_2$ they are preferred.

Intermediate Falloff Range

The extrapolated k_0 and k_∞ values were derived using $F_c = 0.4$ in close agreement with the corresponding $F_c = \exp(-T/342)$ for the reverse reaction.[4]

References

[1] F. Zabel, in Proceedings of the International Conference on Photochemistry, Budapest, August 1987 (to be published).
[2] J. Troe, J. Phys. Chem. **83**, 114 (1979).
[3] R. Simonaitis, S. Glavas, and J. Heicklen, Geophys. Res. Lett. **6**, 385 (1979).
[4] F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, Soc. Faraday Trans. 2 **84**, 569 (1988).

$CCl_3O_2 + NO_2 + M \rightarrow CCl_3O_2NO_2 + M$

$\Delta H° \approx -105$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.2\pm3)\times10^{-29}(T/298)^{-6.0\pm1.5}[O_2]$	233–373	Caralp *et al.*, 1988[1]	(a)

Comments

(a) Pulsed laser photolysis and time-resolved mass spectrometry. Falloff curve measured over the pressure range 1–10 Torr. Falloff extrapolation using $F_c = \exp(-T/260)$. Increasing width of falloff curve included via N from Ref. 2.

Preferred Values

$k_0 = 9.2\times10^{-29}(T/300)^{-6}[N_2]$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

The preferred values are based on the only available data from Ref. 1. $\Delta H°$ was estimated in Ref. 1.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.49\times10^{-11}(T/298)^{-0.3\pm0.3}$	233–373	Caralp *et al.*, 1988[1]	(a)

Comments

(a) See comment for k_0.

Preferred Values

$k_\infty = 1.5\times10^{-11}(T/300)^{-0.3}$ cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the falloff extrapolation from Ref. 1.

Intermediate Falloff Range

The extrapolated k_0 and k_∞ values were obtained using $F_c = \exp(-T/260)$ corresponding to $F_c(300\text{ K}) = 0.32$.

References

[1] F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2 **84**, 569 (1988).

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

$CCl_3O_2NO_2 + M \rightarrow CCl_3O_2 + NO_2 + M$

Low-pressure rate coefficients
Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.6\times10^{-4}\exp(-9310/T)[N_2]$	263–293	Zabel, 1987[1]	(a)
$1.5\times10^{-17}[N_2]$	298*		

Comments

(a) *In situ* production of $CCl_3O_2NO_2$ by UV photolysis of Cl_2–$CHCl_3$–NO_2–O_2–N_2 mixtures. Time dependence of $CCl_3O_2NO_2$ monitored by long path FTIR. Decomposition measured upon addition of large excess of NO to scavenge CCl_3O_2. Pressure range 8–600 Torr. Falloff extrapolation using $F_c = 0.2$; increasing width of falloff curve accounted for by using N from Ref. 2.

Preferred Values

$k_0 = 5.6\times10^{-4}\exp(-9310/T)[N_2]$ s^{-1} over range 260–300 K.

$k_0 = 1.5\times10^{-17}[N_2]$ s^{-1} at 298 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are based on the experiments from Ref. 1, which appear consistent[1] with theoretical models, leading to collision efficiencies of $\beta_c = 0.16$.

High-pressure rate coefficients
Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.42\times10^{16}\exp(-11\,500/T)$	268–298	Simonaitis and Heicklen, 1979[3]	(a)
0.24	298		
$9.1\times10^{14}\exp(-10\,820/T)$	263–293	Zabel, 1987[1]	(b)
0.16	298*		

Comments

(a) Steady-state photolysis of Cl_2–$HCCl_3$–O_2–N_2–NO–NO_2 mixtures at 1 atm. NO decay monitored. Simulation of the mechanism dependent on competition between various Cl-consuming reactions. k assumed to be close to k_∞.

(b) See comment for k_0.

Preferred Values

$k_\infty = 9.1\times10^{14} \exp(-10\,820/T)$ s^{-1} over the range 260–300 K.

$k_\infty = 1.6\times10^{-1}$ s^{-1} at 298 K.

Reliability

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

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

Comments on Preferred Values

Since the experiments from Ref. 1 were based on a direct detection of $CCl_3O_2NO_2$, they are probably less sensitive to uncertain details of the mechanism than the results from Ref. 3. The preferred value, therefore, is based on Ref. 1.

Intermediate Falloff Range

The extrapolated k_0 and k_∞ values were obtained using $F_c = 0.20$. They are lower than the corresponding values $F_c = \exp(-T/260)$ for the reverse reaction used in Ref. 4. Since the F_c values for forward and reverse reactions should be equal, a determination of the equilibrium constant from the rates of the forward and reverse reaction should account for this difference.

References

[1] F. Zabel, in Proceedings of the International Conference on Photochemistry, Budapest, August 1987 (to be published).

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

[3] R. Simonaitis and J. Heicklen, Chem. Phys. Lett. **62**, 473; **68**, 245 (1979).

[4] F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2 **84**, 569 (1988).

$CH_2ClO_2NO_2 + M \rightarrow CH_2ClO_2 + NO_2 + M$

Comments

This reaction has been studied recently[1] using the same technique as for the decomposition of $CH_3O_2NO_2$ and $CH_3CO_3NO_2$ (see this evaluation). Temperatures between 272 and 265 K, pressures between 10 and 800 mbar of N_2 were applied. For 272 K, $k_0 = 1.8\times10^{-20}[N_2]$ s^{-1} and $k_\infty = 0.013$ s^{-1} were obtained using $F_c = 0.4$. For 800 mbar of N_2, $k = 1.36\times10^{16} \exp(-11\,400/T)$ s^{-1} were measured. The results are consistent with data for the decomposition of related nitrates.

References

[1] A. Reimer, K. H. Becker, E. H. Fink, and F. Zabel (to be published).

$O_3 + C_2HCl_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<3\times10^{-20}$	296	Atkinson *et al.*, 1982[1]	(a)

Comments

(a) Decay of O_3 (at initial concentrations of $\lesssim 2.4\times10^{13}$ molecule cm^{-3}) measured in the presence of excess C_2HCl_3 in 1 atm of air, using a chemiluminescence analyzer to monitor O_3.

Preferred Values

$k < 5\times10^{-20}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

Taken from the data of Atkinson *et al.*,[1] with the upper limit being increased by a factor of ca. 2 to take into account additional uncertainties in the study of Atkinson *et al.*[1] This upper limit is consistent with the reported data for the reactions of O_3 with chloroethenes,[2] which show that Cl atom substitution markedly decreases the rate coefficients at room temperature, relative to that for ethene.

References

[1] R. Atkinson, S. M. Aschmann, D. R. Fitz, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **14**, 13 (1982).

[2] R. Atkinson and W. P. L. Carter, Chem. Rev. **84**, 437 (1984).

$O_3 + C_2Cl_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<2\times10^{-23}$	297	Mathias *et al.*, 1974[1]	(a)

Comments

(a) Derived from experiments carried out at initial O_3 and C_2Cl_4 concentrations of $\gtrsim 10^{17}$ molecule cm^{-3} in the presence of excess O_2, using an assumed mechanism and monitoring the formation rate of $COCl_2$. From the data given in Mathias *et al.*,[1] a more conservative upper limit of $k \lesssim 8\times10^{-23}$ cm^3 molecule^{-1} s^{-1} can be derived by assuming that only one $COCl_2$ molecule is formed per C_2Cl_4 reacting.

Preferred Values

$k < 10^{-21}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

Derived from the very limited amount of data reported by Mathias *et al.*,[1] with the upper limit to the rate coefficient being increased by a factor of 50 over that reported [see also comment (a) above]. This upper limit to the rate coefficient for C_2Cl_4 is consistent with the kinetic data for the other chloroethenes,[2] which show that Cl atom substitution markedly decreases the reactivity of the chloroethenes towards O_3, compared to that for ethene.

References

[1] E. Mathias, E. Sanhueza, I. C. Hisatsune, and J. Heicklen, Can. J. Chem. **52**, 3852 (1974).
[2] R. Atkinson and W. P. L. Carter, Chem. Rev. **84**, 437 (1984).

HOCl + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$HOCl + h\nu \rightarrow HCl + O(^3P)$	(1)	230	520
$\rightarrow OH + Cl$	(2)	234	511
$\rightarrow ClO + H$	(3)	393	304
$\rightarrow HCl + O(^1D)$	(4)	419	286

Absorption cross-section data

Wavelength range/nm	Reference	Comments
240–390	Mishalanie *et al.*, 1986[1]	(a)

Comments

(a) Absorption spectra recorded in a 20 m long-path cell interfaced to a low-pressure discharge flow system coupled to a mass spectrometer. A dynamic source of HOCl was obtained by bubbling a Cl_2–He mixture through aqueous $NaHCO_3$. Cl_2 was the major impurity; Cl_2O and OClO gave minimal spectra contamination.

Preferred Values

Absorption Cross Sections

The preferred values are unchanged from values tabulated in the CODATA Supplement I[2] and are based on the work of Knauth *et al.*[3] and Molina *et al.*[4]

Quantum Yields

$\Phi_2 = 1.0$ for $1 > 200$ nm.

Comments on Preferred Values

The new data are significantly lower than the cross sections reported by Knauth *et al.*[3] and Molina *et al.*[4] at $335 < \lambda < 390$ nm and significantly greater than those reported by Knauth *et al.*[3] in the range $240 < \lambda < 330$ where the correction due to Cl_2O impurity has been a source of uncertainty in previous work. At the shorter wavelengths the new values agree with the values originally reported by Molina *et al.*[4] which were later corrected by using a revised equilibrium constant for $2HOCl \rightarrow Cl_2O + H_2O$. The discrepancy between the new studies and the earlier work is difficult to understand, and the possible explanations that the authors offer are not sufficiently compelling to change the recommendation. The large cross sections obtained in the new work, if correct, would decrease the photolysis lifetime by up to 20% in the 28–34 km altitude.

References

[1] E. A. Mishalanie, C. J. Rutkowski, R. S. Hutte, and J. W. Birks, J. Phys. Chem. **90**, 5578 (1986).
[2] CODATA Supplement I, 1982 (see References in Introduction).
[3] H.-D. Knauth, H. Alberti, and H. Clausen, J. Phys. Chem. **83**, 1604 (1979).
[4] M. J. Molina and L. T. Molina, J. Phys. Chem. **82**, 2410 (1978).

$OClO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$OClO + h\nu \rightarrow ClO + O(^3P)$	(1)	245	488
$\rightarrow ClO + O(^1D)$	(2)	435	275

Absorption cross-section data

Wavelength range/nm	Reference	Comments
≃476	Coon, DeWarnes, and Loyd, 1962[1]	(a)
351.5	Clyne and Coxon, 1968[2]	(b)
351.5	Basco and Dogra, 1971[3]	(c)
125–200	Basco and Morse, 1974[4]	(d)
300–464	Birks *et al.*, 1977[5]	(e)
240–480	Wahner, Tyndall, and Ravishankara, 1987[6]	(f)

Comments

(a) Cross sections measured in a few bands near the origin of the $A\,^2A_2\ X\,^2B_1$ transition.

(b) Cross sections measured at 351.5 nm [band head of $a(11)$ band in the $A\,^2A_2\,X\,^2B_1$ system] in a flow system used for kinetics studies.

(c) Cross sections measured at 351.5 nm from absorption in a 0.5 m cell.

(d) Cross sections measured for several bands of the C-X, D-X, and E-X systems of OClO in the vacuum ultraviolet.

(e) Absorption spectrum measured between 300 and 464 nm using scanning spectrometer, but absolute cross section not measured.

(f) Absorption spectrum measured using diode array spectrometer at 204, 296, and 378 K. Absolute cross sections determined by two independent methods for OClO concentration measurements.

Preferred Values

Absorption cross sections at 296 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
475.53	13	329.22	974
461.15	17	322.78	791
446.41	69	317.21	618
432.81	166	311.53	435
420.58	304	305.99	312
408.83	479	300.87	219
397.76	670	296.42	160
387.37	844	291.77	114
377.44	992	287.80	86
368.30	1136	283.51	72
359.73	1219	279.64	60
351.30	1275	275.74	46
343.44	1230	272.93	33
336.08	1139		

Quantum Yields

$\Phi_1 = 1.0$ throughout range 240–495 nm.

Comments on Preferred Values

The spectrum of OClO is characterized by a series of vibronic bands extending from 480 nm down to 270 nm, assigned to the $A\,^2A_2$-$X\,^2B_1$ transition. The band systems observed below 200 nm are assigned to Rydberg transitions.[4] The spectroscopy of the molecule has been studied extensively and the quantum yield for dissociation via reaction (1) appears to be unity throughout the wavelength range 240–495 nm (see discussion by Watson[7]). The various measurements of the cross section are in good agreement, taking into account the expected uncertainties. The most recent measurements of Warner *et al.*[6] were conducted with specific attention to accurate cross-section determinations over a large temperature range and form the basis of our recommendation. The values listed are the experimental values from this study at 296 K. The bands became appreciably sharper with decreasing temperature: The cross sections for the $a(11)$ band at 351.3 nm at 204 and 378 K were 1.531×10^{-17} cm^2 and 0.989×10^{-17} cm^2, respectively. However, the integrated band intensities remained constant for all bands between 204 and 296 K, and therefore, the solar photolysis rate is not expected to have significant temperature dependence.

References

[12] J. B. Coon, R. E. DeWarnes, and C. M. Loyd, J. Mol. Spectrosc. **8**, 285 (1962).
[2] M. A. A. Clyne and J. A. Coxon, Proc. Roy. Soc. London Ser. A **303**, 207 (1968).
[3] N. Basco and S. K. Dogra, Proc. Roy. Soc. London Ser. A **323**, 29 (1971).
[4] N. Basco and R. D. Morse, *Proc. Roy. Soc. London Ser. A* **336**, 495 (1974).
[5] J. W. Birks, B. Shoemaker, T. J. Leck, R. A. Borders, and L. J. Hart, J. Chem. Phys. **66**, 4591 (1977).
[6] A. Wahner, G. S. Tyndall, and A. R. Ravishankara, J. Phys. Chem. **91**, 2734 (1987).
[7] R. T. Watson, J. Phys. Chem. Ref. Data **6**, 871 (1977).

$Cl_2O_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$Cl_2O_2 + h\nu \rightarrow ClO + ClO$	(1)	72.5	1649
$\rightarrow Cl + ClOO$	(2)	85	1407
$\rightarrow Cl + OClO$	(3)	94	1272
$\rightarrow Cl_2 + O_2$	(4)	− 131.4	···

Absorption cross-section data

Wavelength range/nm	Reference	Comments
232–292	Basco and Hunt, 1979[1]	(a)
200–380	Molina and Molina, 1987[2]	(b)
220–360	Cox and Hayman, 1987[3]	(c)

Comments

(a) Flash photolysis of Cl_2O and OClO at room temperature; residual absorption observed during decay of ClO at 298 K assigned to Cl_2O_2. Cross sections based on mass balance during ClO decay and absolute cross sections for ClO, Cl_2O, and OClO.

(b) Reaction between Cl and OClO at 240 K in a fast flow system. Residual UV spectrum of flowing mixture assigned to ClOOCl, on basis of IR spectra of the mixture. Cross sections based on mass balance of ClO_x.

(c) Steady-state photolysis of Cl_2/Cl_2O mixtures. Residual spectra assignment to Cl_2O_2 based on time, temperature, and [ClO] dependence. Same spectrum observed in Cl_2/O_3 mixtures but not when OClO was used as a source of ClO. Absorption cross section from mass balance of ClO_x at temperatures of 233 and 265 K.

Quantum yield data

Measurement	λ/nm	Reference	Comments
$\Phi_2 \simeq 1$	254	Cox and Hayman, 1988[3]	(a)

Comments

(a) Photolysis of Cl_2O/N_2 mixtures at 203–233 K. Steady-state analysis of Cl_2O_2 concentration-time behavior.

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
350	< 10	280	180
340	12	270	260
330	20	260	430
320	36	250	620
310	60	240	580
300	88	230	330
290	130	220	180

Quantum Yields

No recommendation.

Comments on Preferred Values

The reported absorption spectra for Cl_2O_2 are shown in Fig. 4. There is considerable disagreement between them, except in the wavelength region > 300 nm, where the cross sections reported by Molina and Molina[2] and Cox and Hayman[3] agree quite well. The residual absorption observed in the steady-state experiments of Cox and Hayman behaves in the expected way for a ClO dimer of structure ClOOCl. On the other hand, Molina and Molina argue that their IR data obtained in the same conditions supports assignment of their UV spectrum to the ClO dimer in the predominant form. Cox and Hayman observe residual spectra similar to that of Molina and Molina,[2] but only when OClO is present. They tentatively assign this to the Cl_2O_3 molecule. The assign-

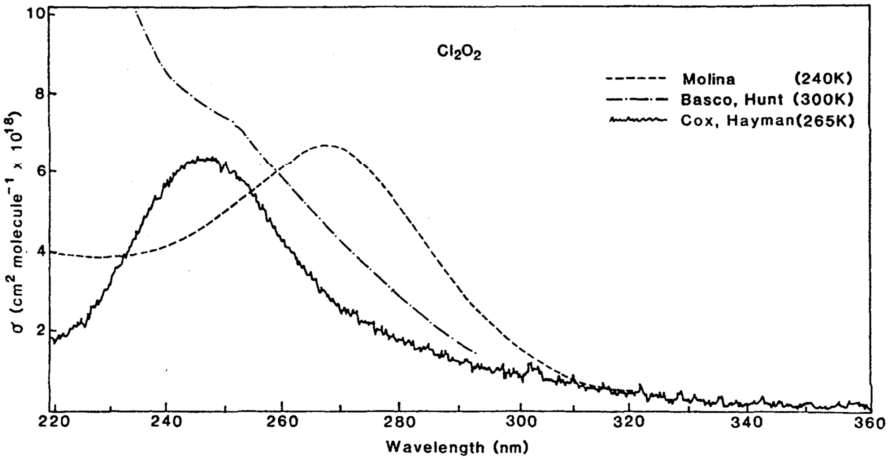

FIG. 4. Absorption cross section of Cl_2O_2, 220–360 nm.

ment of Cox and Hayman seems to be the more soundly based, and their cross sections form the basis of a tentative recommendation. The actual values differ only marginally from those given by Molina and Molina at $\lambda > 300$ nm, which may be due to Cl_2O_3.

The continuous nature of the Cl_2O_2 absorption suggests efficient photodissociation ($\Phi = 1$), which is consistent with the interpretation of the steady-state photolysis experiments of Cox and Hayman.[3] Margitan[4] reports evidence for Cl production in the photolysis of Cl_2O_2 formed by ClO recombination in a discharge flow system. There are sufficient experimental data to form the basis of a recommendation.

References

[1]N. Basco and J. E. Hunt, Int. J. Chem. Kinet. **11**, 649 (1979).
[2]L. T. Molina and M. J. Molina, J. Phys. Chem. **91**, 433 (1987).
[3]R. A. Cox and G. D. Hayman, Nature **332**, 796 (1988).
[4]J. J. Margitan, J Geophys. Res. **88** (C9), 5418 (1983).

4.8. Bromine Species

$Br + HO_2 \rightarrow HBr + O_2$

$\Delta H^\circ = -162.8$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.6 \pm 0.9) \times 10^{-13}$	298	Poulet, Laverdet, and Le Bras, 1984[1]	(a)
$(1.4 \pm 0.2) \times 10^{-11} \exp[-(590 \pm 140)/T]$	260–390	Toohey, Brune, and Anderson, 1987[2]	(b)
$(2.0 \pm 0.3) \times 10^{-12}$	298		
Reviews and Evaluations			
8.0×10^{-13}	298	NASA, 1985[3]	(c)
$1.5 \times 10^{-11} \exp(-600/T)$	200–300	NASA, 1987[4]	(d)

Comments

(a) Discharge flow–LIF/MS for detection of reactive species. $Br_2/HCHO/O_2$ system. $k(Br + HCO)$ determined simultaneously by comparison of results with computer simulation using assumed chemical model. HO_2 determined by titration with NO to produce OH/NO_2.

(b) Discharge flow–LMR detection of HO_2, RF detection of Br. k determined from HO_2 decays in presence of excess Br.

(c) Based on the value of Poulet *et al.*[1]

(d) Based on results of Toohey *et al.*[2]

Preferred Values

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

$k = 1.4 \times 10^{-11} \exp(-590/T)$ cm^3 molecule^{-1} s^{-1} in the range 260–390 K.

Reliability

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

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

Comments on Preferred Values

Toohey *et al.*[2] report a value of $k_{295} = 2.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, which is nearly a factor of 3 higher than that of Poulet *et al.*[1] Since both Br and HO_2 were detected directly, and no modeling was necessary to extract the rate constant, the expression of Toohey *et al.* is favored.

References

[1] G. Poulet, G. Laverdet, and G. Le Bras, J. Chem Phys. **80**, 1922 (1984).
[2] D. W. Toohey, W. M. Brune, and J. G. Anderson, J. Phys. Chem. **91**, 1215 (1987).
[3] NASA Evaluation No. 7, 1985 (see References in Introduction).
[4] NASA Evaluation No. 8, 1987 (see References in Introduction).

$Br + H_2O_2 \rightarrow HBr + HO_2$ (1)
$\rightarrow HOBr + HO$ (2)

$\Delta H^\circ(1) = 2.7$ kJ mol^{-1}
$\Delta H^\circ(2) = -16$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<5 \times 10^{-16}$	298	Toohey, Brune, and Anderson, 1987[1]	(a)
$<5 \times 10^{-16}$	378		
Reviews and Evaluations			
$<2 \times 10^{-15}$	298	CODATA, 1982[2]	(b)
$<1 \times 10^{-11} \exp[-(2500/T)]$	200–300	NASA, 1985[3]	(b)
$<1 \times 10^{-11} \exp[-(3000/T)]$	200–300	NASA, 1987[4]	(c)

Comments

(a) Discharge flow–resonance fluorescence detection of bromine atoms. Decays of bromine atoms monitored in the presence of excess H_2O_2. Attempted measurement of HO_2 and OH products (LMR) allows upper limits of 5×10^{-16} cm^3 molecule^{-1} s^{-1} to be quoted for either channel (1) or (2).

(b) Based on the results of Leu[5] and Posey *et al.*[6]

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

Preferred Value

$k < 5 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

Upper limit based on the data of Toohey *et al.*,[1] who also obtained the same upper limit at 378 K.

References

[1] D. W. Toohey, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **91**, 1215 (1987).
[2] CODATA Supplement I, 1982 (see References in Introduction).
[3] NASA Evaluation No. 7, 1985 (see References in Introduction).
[4] NASA Evaluation No. 8, 1987 (see References in Introduction).
[5] M.-T. Leu, Chem. Phys. Lett. **69**, 37 (1980).
[6] J. Posey, J. Sherwell, and M. Kaufman, Chem. Phys. Lett. **77**, 476 (1981).

$Br + O_3 \rightarrow BrO + O_2$

$\Delta H^\circ = -130$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.42 \pm 0.03) \times 10^{-12}$	298	Toohey, Brune, and Anderson, 1988[1]	(a)
$(3.28 \pm 0.40) \times 10^{-11} \exp[-(944 \pm 30)/T]$	248–418		
Reviews and Evaluations			
$1.4 \times 10^{-11} \exp(-760/T)$	220–360	CODATA, 1984[2]	(b)
$1.4 \times 10^{-11} \exp(-755/T)$	200–300	NASA, 1985[3]	(b)
$1.7 \times 10^{-11} \exp(-800/T)$	200–300	NASA, 1987[4]	(c)

Comments

(a) Discharge flow–resonance fluorescence detection of Br atoms. Measurements made in 1–3 Torr He. Decay of Br atoms in the presence of excess O_3 monitored.

(b) Based on the data of Clyne and Watson,[5] Leu and DeMore,[6] Michael *et al.*,[7] and Michael and Payne.[8]

(c) Based on the data of Clyne and Watson,[5] Leu and

DeMore,[6] Michael *et al.*,[7] Michael and Payne,[8] and Toohey *et al.*[1]

Preferred Values

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

$k = 1.7\times10^{-11}\exp(-800/T)$ cm^3 molecule^{-1} s^{-1} over range 220–360 K.

Reliability

$\Delta \log k = \pm 0.1$.

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

Comments on Preferred Values

The results reported for k at 298 K in Refs. 1 and 5–8 are in good agreement, and the preferred value is the mean of these five values. The reported temperature dependences are not in such good agreement with a spread of 25% in k at 220 K and 65% at 360 K. The preferred temperature dependence is the mean of the (E/R) values reported in Refs. 1 and 6–8.

References

[1] D. W. Toohey, W. H. Brune, and J. G. Anderson, Int. J. Chem. Kinet. **20**, 131 (1988).
[2] CODATA Supplement II, 1984 (see References in Introduction).
[3] NASA Evaluation No. 7, 1985 (see References in Introduction).
[4] NASA Evaluation No. 8, 1987 (see References in Introduction).
[5] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 **71**, 336 (1975).
[6] M. T. Leu and W. B. DeMore, Chem. Phys. Lett. **48**, 317 (1977).
[7] J. V. Michael, J. H. Lee, W. A. Payne, and L. J. Stief, J. Chem. Phys. **68**, 4093 (1978).
[8] J. V. Michael and W. A. Payne, Int. J. Chem. Kinet. **11**, 799 (1979).

$Br + CH_3CHO \rightarrow HBr + CH_3CO$

$\Delta H° = -67.4$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5\pm0.5)\times10^{-12}$	300	Islam, Marshall, and Benson, 1984[1]	(a)
Relative Rate Coefficients			
$(3.7\pm0.1)\times10^{-12}$	298	Niki *et al.*, 1985[2]	(b)

Comments

(a) Very low pressure reactor study. Br atoms generated by microwave discharge of Br_2 in helium, with mass spectrometric detection of reactants and products.

(b) Br atoms generated by photolysis of Br_2 at 350–600 nm in 700 Torr total pressure of N_2. Rate coefficient determined relative to that for the reaction of Br atoms with HCHO, with $k(Br + CH_3CHO)/k(Br + HCHO) = 3.39\pm0.10$. Placed on an absolute basis by use of $k(Br + HCHO) = 1.1\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[3–5]

Preferred Values

$k = 3.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The two studies are in excellent agreement, and the preferred value is the mean of the two rate coefficients measured.

References

[1] T. S. A. Islam, R. M. Marshall, and S. W. Benson, Int. J. Chem. Kinet. **16**, 1161 (1984).
[2] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **17**, 525 (1985).
[3] CODATA, Supplement II, 1984 (see References in Introduction).
[4] NASA Evaluation No. 7, 1985 (see References in Introduction).
[5] NASA Evaluation No. 8, 1987 (see References in Introduction).

$Br + OClO \rightarrow BrO + ClO$

$\Delta H^\circ = 14$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.2 \pm 0.5) \times 10^{-14}$	300	Clyne and Coxon, 1967[1]	(a)
$(4.2^{+0.8}_{-0.4}) \times 10^{-13}$	298	Clyne and Watson, 1975[2]	(b)
$2.4 \times 10^{-11} \exp(-1320 \pm 20/T)$	298–430	Toohey, Brune, and Anderson, 1987[3]	(c)
2.9×10^{-13}	298		
Reviews and Evaluations			
4.2×10^{-13}	298	Watson, 1977[4]	(d)

Comments

(a) Discharge flow–UV absorption detection of OClO. High concentrations of Br and OClO in second-order kinetic conditions.

(b) Discharge flow–mass spectrometric detection of OClO decay in excess Br. Decays were first order, and computer fitting was used to compensate for reverse reaction.

(c) Discharge flow–resonance fluorescence detection of Br decay in excess OClO.

(d) Based on data of Clyne and Watson.[2]

Preferred Values

$k = 3.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.6 \times 10^{-11} \exp(-1300/T)$ cm^3 molecule^{-1} s^{-1} over range 200–450 K.

Reliability

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

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

Comments on Preferred Values

The preferred value at 298 K is the mean of the values reported by Clyne and Watson[2] and Toohey *et al.*[3] Both these studies required correction for the effect of the reverse reaction on the decay, which was not taken into account in the earlier study of Clyne and Coxon, which is therefore disregarded. The temperature dependence of Toohey *et al.* is accepted.

References

[1] M. A. A. Clyne and J. A. Coxon, Proc. R. Soc. London Ser. A **298**, 424 (1967).

[2] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 **73**, 1169 (1977).

[3] D. W. Toohey, W. H. Brune, and J. G. Anderson, J. Phys. Chem. (to be published).

[4] R. T. Watson, J. Phys. Chem. Ref. Data **36**, 892 (1977).

$HO + HBr \rightarrow H_2O + Br$

$\Delta H^\circ = -132.9$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.12 \pm 0.045) \times 10^{-11}$	298	Cannon *et al.*, 1984[1]	(a)
$(1.1 \pm 0.1) \times 10^{-11}$	298	Ravishankara, Wine, and Wells, 1985[2]	(b)
Reviews and Evaluations			
8.0×10^{-12}	249–416	CODATA, 1984[3]	(c)
1.1×10^{-11}	200–300	NASA, 1985[4]	(d)
1.1×10^{-11}	200–300	NASA, 1987[5]	(e)

Comments

(a) FP–LIF technique.

(b) LFP–RF, LFP–LIF techniques gave values of $(11.4 \pm 0.3) \times 10^{-12}$ and $(10.7 \pm 0.3) \times 10^{-12}$, respectively.

(c) Based on the results of Takacs and Glass,[6] Ravishankara *et al.*,[7] Jourdain *et al.*,[8] and Husain *et al.*[9]

(d) Based on the results of Ravishankara *et al.*,[7] Jourdain *et al.*,[8] and Cannon *et al.*[1]

(e) Based on the results cited in (d) and Ravishankara *et al.*[2]

Preferred Value

$k = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 249–416 K.

Reliability

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

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

Comments on Preferred Value

Preferred value is based on the results of Ravishankara *et al.*,[7] Jourdain *et al.*,[8] Cannon *et al.*,[1] and Ravishankara *et al.*,[2] with the temperature independence based on the results of Ravishankara *et al.*[7] Ravishankara *et al.*[2] monitored HBr in the UV and have suggested that HBr adsorption on surfaces might be source of error in the lower determinations.

References

[1] B. D. Cannon, J. S. Robertshaw, I. W. M. Smith, and M. D. Williams, Chem. Phys. Lett. **105**, 380 (1984).
[2] A. R. Ravishankara, P. H. Wine, and J. R. Wells, J. Chem. Phys. **83**, 447 (1985).
[3] CODATA Supplement II, 1984 (see References in Introduction).
[4] NASA Evaluation No. 7, 1985 (see References in Introduction).
[5] NASA Evaluation No. 8, 1987 (see References in Introduction).
[6] G. A. Takacs and G. P. Glass, J. Phys. Chem. **77**, 1060 (1973).
[7] A. R. Ravishankara, P. H. Wine, and A. O. Langford, Chem. Phys. Lett. **63**, 479 (1979).
[8] J. L. Jourdain, G. Le Bras, and J. Combourieu, Chem. Phys. Lett. **78**, 483 (1981).
[9] D. Husain, J. M. C. Plane, and N. K. H. Slater, J. Chem. Soc. Faraday Trans. 2 **77**, 1949 (1981).

$HO + Br_2 \rightarrow HOBr + Br$

$\Delta H^\circ = -38$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.28 \pm 0.5) \times 10^{-11}$	298	Loewenstein and Anderson, 1984[1]	(a)
$(3.4 \pm 1.2) \times 10^{-11}$	262–303	Boodaghians, Hall, and Wayne, 1987[2]	(b)
$1.35 \times 10^{-11} \exp(400/T)$	260–360	Toohey, Brune, and Anderson, 1988[3]	(c)
5.2×10^{-11}	298		
Reviews and Evaluations			
4.2×10^{-11}	298	CODATA, 1984[4]	(d)
4.8×10^{-11}	298	NASA, 1985[5]	(e)
4.2×10^{-11}	200–300	NASA, 1987[6]	(f)

Comments

(a) Discharge flow–resonance fluorescence technique.

(b) Discharge flow–resonance fluorescence technique.

(c) Discharge flow–LMR detection of OH radicals. k_{298} calculated here from temperature-dependent expression.

(d) Based on the discharge flow–EPR/LIF measurement of Poulet *et al.*[7]

(e) Based on the results of Poulet *et al.*[7] and Loewenstein and Anderson.[1]

(f) Based on the results cited in (e) and Boodaghians *et al.*[2]

Preferred Values

$k = 4.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.2 \times 10^{-11} \exp(400/T)$ cm^3 molecule^{-1} s^{-1} over range 260–360 K.

Reliability

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

$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

k reasonably well determined near 298 K. Boodaghians *et al.*[2] measured k for the temperature range 262–303 K and found a near zero dependence. In contrast the recent data of Toohey *et al.*[3] display a significant negative temperature dependence in the range 260–360 K. The latter result is preferred and the recommendation is based on this study.

References

[1] L. M. Loewenstein and J. G. Anderson, J. Phys. Chem. **88**, 6277 (1984).
[2] R. B. Boodaghians, I. W. Hall, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2 **83**, 529 (1987).
[3] D. W. Toohey, W. H. Brune, and J. G. Anderson, J. Phys. Chem. (to be published).
[4] CODATA Supplement II. 1984 (see References in Introduction).
[5] NASA Evaluation No. 7, 1985 (see References in Introduction).
[6] NASA Evaluation No. 8, 1987 (see References in Introduction).
[7] G. Poulet, G. Laverdet, and G. Le Bras, Chem. Phys. Lett. **94**, 129 (1983).

$$\begin{aligned} BrO + ClO &\rightarrow Br + OClO \quad &(1)\\ &\rightarrow Br + ClOO \quad &(2)\\ &\rightarrow BrCl + O_2 \quad &(3)\end{aligned}$$

$\Delta H^\circ(1) = -14$ kJ mol^{-1}
$\Delta H^\circ(2) = -20$ kJ mol^{-1}
$\Delta H^\circ(3) = -212$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.2 \pm 1.0) \times 10^{-12}$	241–408	Hills *et al.*, 1987[1]	(a)
$(1.4 \pm 0.2) \times 10^{-11}$	298	Toohey and Anderson, 1988[2]	(b)
$6.1 \times 10^{-12} \exp[(240 \pm 60)/T]$	220–400	Sander and Friedl, 1988[3]	(c)
$(1.29 \pm 0.18) \times 10^{-11}$	298		
$4.7 \times 10^{-12} \exp[(320 \pm 60)/T]$	220–400	Friedl and Sander, 1988[4]	(d)
$(1.29 \pm 0.18) \times 10^{-11}$	296		
$k_1 = 5.1 \pm 1.1 \times 10^{-12}$	287	Bennett, Cox, and Hayman, 1987[5]	(e)
$k_3 = 1.4 \pm 0.7 \times 10^{-12}$			
Branching Ratios			
$k_1/k = 0.55 \pm 0.10$	241–305	Hills *et al.*, 1987[1]	(f)
$k_2/k = 0.45 \pm 0.10$			
$k_3/k \leqslant 0.02$			
$k_1/k = 0.45$	298	Toohey and Anderson, 1988[2]	(b)
$k_3/k = 0.05$–0.17	298		
$k_1/k = 0.68 \pm 0.10$	220	Sander and Friedl, 1988[3]	(g)
$k_1/k = 0.59 \pm 0.10$	298		
$k_1/k = 0.55 \pm 0.07$; $k_2/k = 0.39 \pm 0.10$; $k_3/k = 0.06 \pm 0.03$	220	Friedl and Sander, 1988[4]	(h)
$k_1/k = 0.48 \pm 0.07$; $k_2/k = 0.40 \pm 0.10$; $k_3/k = 0.08 \pm 0.03$	298		
$k_1/k = 0.44 \pm 0.07$; $k_2/k = 0.44 \pm 0.11$; $k_3/k = 0.08 \pm 0.03$	400		
Reviews and Evaluations			
$k_1 = 6.7 \times 10^{-12}$	300	Watson, 1977[6]	(i)
$k_2 = 6.7 \times 10^{-12}$			
$k_1 = 6.7 \times 10^{-12}$	298	CODATA, 1984[7]	(i)
$k_2 + k_3 = 6.7 \times 10^{-12}$			
$k_1 = 6.7 \times 10^{-12}$	200–300	NASA, 1985[8]; NASA, 1987[9]	(i) (j)
$k_2 = 6.7 \times 10^{-12}$			

Comments

(a) Discharge flow–mass spectrometric detection of BrO, ClO, OClO, and BrCl. Pseudo-first-order decay of BrO in excess ClO.

(b) Discharge flow–resonance fluorescence detection of Cl and Br. BrO is determined by conversion to Br by reaction with NO. ClO by laser magnetic resonance. 298 K value is determined from ClO decay in excess BrO. k_1 value from ClO loss in presence of excess BrO and O_3. Authors suggest that BrCl is formed in excited $^3\pi$ state, which may rapidly decompose to Cl + Br, unless quenched by collisions with Br_2, etc. The range of values for k_3/k applies to the experimental conditions covered in their study, and depends on the concentration of Br_2 and other quenchers.

(c) Flash photolysis–long path UV absorption detection of BrO, ClO, and OClO. BrO decay monitored with $[ClO] \geqslant [BrO]$ in flash photolysis of Br_2/Cl_2O mixtures. Cross sections of BrO and ClO measured in the same study; $\sigma(ClO) = 8.36 \pm 1.02 \times 10^{-18}$ cm^2 molecule^{-1} at 277.5 nm and 298 K: $\sigma(BrO) = 1.71 \times 10^{-17}$ cm^2 molecule^{-1} at 338.5 nm and 298 K. Both cross sections increased with decreasing temperature, being, respectively, 20% and 29% higher at 220 K.

(d) Discharge flow–mass spectrometric detection of BrO, ClO, OClO, and BrCl. BrO decay monitored in excess [ClO]. ClO produced by reaction of Cl with Cl_2O or OClO. BrO from Br + O_3 or O + Br_2 reaction.

(e) Molecular modulation–UV absorption detection of BrO and OClO at 338 nm and 351.5 nm, respectively. Time-resolved measurement of OClO production and BrO loss in photolysis of $Cl_2/Br_2/O_3/N_2$ mixtures at 1 atm pressure. [BrO] based on value of $\sigma(BrO) = 1.7 \times 10^{-17}$ cm^2 molecule^{-1} at 339 nm. Computer fit to complex kinetics. k_3 depends on $k(BrO + BrO \rightarrow Br_2 + O_2)$ for which a value of 6.5×10^{-13} cm^3 molecule^{-1} s^{-1} determined in the same study was used.

(f) As (a); channel (1) from measurement of Δ[OClO]/Δ[ClO]; channel (2) from conversion of Cl to BrCl by reaction with excess Br_2; channel (3) from apparent absence of BrCl in the absence of Br_2.

(g) As (c); based on Δ[OClO]/Δ[BrO] as a function of reaction time.

(h) As (d); based on yields of OClO, Cl (by conversion to BrCl) and BrCl, and the loss of BrO and ClO.

(i) Based on data of Clyne and Watson.[10] Earlier result of Basco and Dogra[11] was rejected due to erroneous analysis of the kinetic data (see Ref. 10).

(j) Based on data of Clyne and Watson,[10] Toohey *et al.*,[2] Friedl and Sander[3,4] and the temperature independence of Hills *et al.*[1]

Preferred Values

$k_1 = 6.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2 + k_3 = 6.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 1.9\times10^{-12}\exp(390/T)$ over range 200–400 K.

$k_2 + k_3 = 3.9\times10^{-12}\exp(140/T)$ over range 200–400 K.

Reliability

$\Delta \log k_1 = \pm 0.1$ at 298 K; $\Delta \log (k_2 + k_3) = \pm 0.1$ at 298 K.

$\Delta (E/R)_1 = \pm 400$ K; $\Delta (E/R)_{2+3} = \pm 200$ K.

Comments on Preferred Values

There have been several new studies of this reaction that generally show excellent agreement with the earlier 298 K mass spectrometric study of Clyne and Watson.[10] The exception is the result of Hills *et al.*[1] which is 25%–40% lower in the overall rate coefficient. Friedl and Sander[3,4] report a negative temperature dependence from two independent studies using discharge flow–mass spectrometry and flash photolysis–UV absorption, while Hills *et al.* report no significant temperature dependence between 241 and 408 K. Negative temperature dependences are usually observed for exothermic reactions between small radicals, and the results of Friedl and Sander are accepted on this basis.

The branching ratios k_1/k determined at 298 K, including the earlier data of Clyne and Watson, all lie in the range 0.45 to 0.59. The preferred value of k_1 at 298 K is based on a value of $k_1/k = 0.52$ and the mean of the values for the overall rate at 298 K measured by Sander and Friedl (both methods), Toohey *et al.* and Clyne and Watson. The data of Bennett *et al.*, in which only k_1 was determined, are also consistent with this value, considering the larger errors associated with their study. The data of Friedl and Sander show a distinct temperature dependence with k_1/k increasing with decreasing temperature; a value of $k_1/k = 0.61$ is obtained by averaging the 220 K data of Sander and Friedl[3] and Friedl and Sander.[4] This forms the basis of the temperature dependencies of k_1 and $k_2 + k_3$, using the following expression for the overall rate constant: $k = 5.2\times10^{-12}\exp(280/T)$, obtained from the mean 298 K value and the average E/R from the two independent studies of Friedl and Sander. The uncertainties cover the possibility that k and k_1 are independent of temperature.

Friedl and Sander[4] have observed BrCl production but Hills *et al.*[1] observed no BrCl when Cl atoms were scavenged to prevent BrCl formation via the rapid reaction of Cl with Br_2. Toohey *et al.*[2] cannot reconcile observed Br atom yields without significant BrCl formation, and the decay of BrO in the experiments of Bennett *et al.*[5] required a channel with no Br production in the BrO + ClO reaction. Thus, there is strong independent evidence that ground-state BrCl can be formed in this reaction, and the arguments of Toohey and Anderson[2] that this may occur through vibrationally excited BrCl($^3\pi_0$) is compelling. Because the fate of excited BrCl formed under stratospheric conditions cannot be stated quantitatively, no recommendation is given for the branching ratio for the BrCl forming channel. The value of $k_3/k = 0.08$, measured by Friedl and Sander is probably the best choice for stratospheric modeling.

References

[1] A. J. Hills, R. J. Cicerone, J. G. Calvert, and J. W. Birks, Nature **328**, 405 (1987); J. Phys. Chem. **92**, 1853 (1988).

[2] D. W. Toohey and J. G. Anderson, J. Phys. Chem. **92**, 1705 (1988).

[3] S. P. Sander and R. Friedl, J. Phys. Chem. (to be published).

[4] R. Friedl and S. P. Sander, J. Phys. Chem. (to be published).

[5] P. Bennett, R. A. Cox, and G. D. Hayman, J. Chem. Soc. Faraday 1 (to be published).

[6] R. T. Watson, J. Phys. Chem. Ref. Data **6**, 871 (1977).

[7] CODATA Supplement II, 1984 (see References in Introduction).

[8] NASA Evaluation No. 7, 1985 (see References in Introduction).

[9] NASA Evaluation No. 8, 1987 (see References in Introduction).

[10] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 **73**, 1169 (1977).

[11] N. Basco and S. K. Dogra, Proc. R. Soc. London Ser. A **323**, 417 (1971).

$BrO + h\nu \rightarrow$ products

Comments

Sander[1] has remeasured the absolute absorption cross section of the $(v' = 7) \leftarrow (v'' = 0)$ band in the $A\,^2\pi - X\,^2\pi$ system at 338.3 nm at a resolution of 0.17 nm and a temperature of 298 K, using flash photolysis of $O_2 + Br_2$ mixtures. The value obtained was $1.7 \pm 0.2\times10^{-17}$ cm^2 molecule^{-1}, which is in excellent agreement with the value obtained by Cox *et al.*,[2] on which the previous evaluation is based. No change is recommended in the preferred values given in CODATA, 1984.[3]

References

[1] S. P. Sander and R. Friedl., J. Phys. Chem. (to be published).

[2] R. A. Cox, D. W. Sheppard, and M. P. Stevens, J. Photochem. **19**, 189 (1982).

[3] CODATA Supplement II, 1984 (see References in Introduction).

4.9. Iodine Species

$I + O_3 \rightarrow IO + O_2$

$\Delta H^\circ = -73$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.6 \pm 3.0) \times 10^{-13}$	303	Jenkin and Cox, 1985[1]	(a)
$(9.5 \pm 1.5) \times 10^{-13}$	298	Sander, 1986[2]	(b)
Reviews and Evaluations			
1.0×10^{-12}	298	CODATA, 1984[3]	(c)

Comments

(a) Photochemical modulation technique with product IO detected by visible absorption. Data analysis involved numerical simulation of observed IO time dependence using an assumed chemical model.

(b) Flash photolysis–visible absorption detection of IO. First-order formation constants for IO measured for a range of excess O_3 concentrations. Rate constant obtained from the asymptotic slope at high O_3 concentrations.

(c) Based on the result of Clyne and Cruse[4] using discharge flow with UV detection of O_3 in the presence of excess atomic iodine.

Preferred Value

$k = 9.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$.

Comments on Preferred Value

The value of $k(I + O_3)$ is reasonably well determined at temperatures near 298 K. Further studies of the temperature dependence of this reaction are required.

References

[1] M. E. Jenkin and R. A. Cox, J. Phys. Chem. **89**, 192 (1985).
[2] S. P. Sander, J. Phys. Chem. **90**, 2194 (1986).
[3] CODATA Supplement I, 1984 (see References in Introduction).
[4] M. A. A. Clyne and H. W. Cruse, Trans. Faraday Soc. **66**, 2227 (1970).

$HO + I_2 \rightarrow HOI + I$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.6^{+1.6}_{-0.8}) \times 10^{-10}$	298	Loewenstein and Anderson, 1985[1]	(a)
Relative Rate Coefficients			
$(2.1 \pm 1.0) \times 10^{-10}$	294	Jenkin, Clemitshaw, and Cox, 1984[2]	(b)

Comments

(a) Discharge flow–resonance fluorescence detection of HO. Reaction studied as a function of pressure and surface/volume. Interference from heterogeneous reactions experienced, but quoted value of $k(I_2 + HO)$ represents homogeneous reaction and is independent of pressure (0.56–5.9 Torr He and 0.51–7.75 Torr Ar).

(b) Steady-state photolysis system. HO concentrations inferred from the rate of disappearance of C_2H_4, and determined as a function of I_2 concentration, $k(I_2 + HO)$ therefore measured relative to $k(C_2H_4 + HO) = 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Measurements made at 760 Torr.

Preferred Value

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

Reliability

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

Comments on Preferred Value

The two reported values agree well considering the quoted error limits. The preferred value is the mean of the two studies.

References

[1] L. M. Loewenstein and J. G. Anderson, J. Phys. Chem. **89**, 5371 (1985).
[2] M. E. Jenkin, K. C. Clemitshaw, and R. A. Cox, J. Chem. Soc. Faraday Trans. 2 **80**, 1633 (1984).

$$\begin{aligned} IO + IO &\rightarrow I_2 + O_2 && (1)\\ &\rightarrow 2I + O_2 && (2)\\ &\rightarrow I + OIO && (3)\\ IO + IO + M &\rightarrow I_2O_2 + M && (4) \end{aligned}$$

$\Delta H^\circ(1) = -138$ kJ mol^{-1}
$\Delta H^\circ(2) = -290$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k' = (8.0 \pm 2.7)\times10^{-12} + (5.6 \pm 0.8)\times10^{-30}[N_2]$	277	Jenkin and Cox, 1985[1]	(a) (b)
$1.73\times10^{-12}\exp[(1020 \pm 200)/T]$	250–373	Sander, 1986[2]	(c)
$(5.6 \pm 1.2)\times10^{-11}$	298		
$k' = (2.5 \pm 0.5)\times10^{-11} + 1\times10^{-30}[M]$	298	Sander, 1986[2]	(a) (d)
$M = Ar, N_2$			
$(3.0 \pm 0.5)\times10^{-11}$	298	Martin *et al.*, 1987[3]	(e)
$k' = (6.6 \pm 2.0)\times10^{-11}$; $P = 1$ atm N_2	300	Stickel *et al.*, 1988[4]	(a) (f)
Branching Ratio			
$k_2/k_4[M] \leqslant (0.25 \pm 0.11)$	295	Jenkin, Cox, and Candeland, 1985[5]	(g)
Pressure = 1 atm			
$k_1/k < 0.05$	298	Sander, 1986[2]	(h)
Reviews and Evaluations			
3.0×10^{-12}	298	CODATA, 1982[6]	(i)

Comments

(a) In systems where IO is produced in the presence of excess O_3, the occurrence of channels (2) and (3) will regenerate IO by the reaction $I + O_3$ and hence the measured rate coefficient is given by the sum $k' = k_1 + 0.5k_3 + k_4[M]$. This assumes that OIO produced in channel (3) does not decompose rapidly to produce I atoms or IO radicals.

(b) Molecular modulation–visible absorption. IO produced by $I + O_3$ reaction and detected at 426.9 nm. Pressure range 25–404 Torr. σ determined to be 2.2×10^{-17} cm^2 molecule^{-1} (306 K).

(c) Flash photolysis–visible absorption. IO generated from $O + I_2$ reaction. k found to be independent of pressure in the range 20–700 Torr. σ found to be temperature dependent.

(d) Flash photolysis–visible absorption. IO produced by $I + O_3$ reaction. Pressure range 20–700 Torr. $\sigma = 3.1\times10^{-17}$ cm^2 molecule^{-1} (298 K) used to obtain rate constants.

(e) Discharge flow mass spectrometric technique. IO generated from microwave discharge of O_2 in the presence of I_2, and detected indirectly after titration with NO (i.e., NO_2 detected). Pressure = 1 Torr He.

(f) Flash photolysis–visible absorption. IO produced by photolysis of O_3 in the presence of I_2 and detected over the wavelength range 410–470 nm. Pressure = 760 Torr. σ determined to be $(3.1 \pm 0.6)\times10^{-17}$ cm^2 molecule^{-1} at the (4,0) band head (300 K).

(g) Measurement of the iodine atom sensitized decomposition of O_3. O_3 decays measured by chemiluminescence technique. Pressure = 760 Torr. Results allowed estimate of ratio between I-atom-producing channels and non-I-atom-producing channels, with channel (1) assumed negligible, and channel (3) not considered. Inclusion of channel (3) would suggest that $(k_2 + 0.5k_3)/(k_4[M] + 0.5k_3) \leqslant (0.25 \pm 0.11)$.

(h) I_2 measured by visible absorption during $O + I_2$ experiments. No regeneration of I_2 detected on timescale of IO disappearance, leading to quoted upper limit.

(i) Based on the discharge flow results of Clyne and Cruse.[7] IO produced from $I + O_3$ reaction at 1 Torr pressure.

Preferred Values

$k = 5.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K at 1 atm pressure.

$k = 1.7\times10^{-12}\exp(1020/T)$ cm^3 molecule^{-1} s^{-1} over range 250–373 K at 1 atm pressure.

Reliability

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

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

Comments on Preferred Values

Difficulties in studying this reaction have been experienced owing to poor knowledge of σ (Ref. 7) and also because of problems associated with wall reactions and aerosol products.[1,8] It is apparent that the reaction proceeds by several channels, and it is believed that the results from systems where IO is produced in the absence of O_3 from the $O + I_2$ reaction give the overall value of $k(= k_1 + k_2 + k_3 + k_4[M])$. The preferred values are based on the results of Sander[2] for the temperature range 250–373 K. Sander found that k was independent of pressure and postulated that reaction channels (1), (2), and (4) proceed via a common excited IOOI dimer, which is consistent with the negative temperature dependence. The low-pressure measurement of Martin *et al.*[3] using the reaction of $O + I_2$ to generate IO in the absence of O_3 provides a value of k at 298 K, which is 40% lower than the preferred value, but lies within the stated uncertainty limits.

The results of Jenkin and Cox,[1] Sander,[2] Clyne and Cruse,[7] and Cox and Coker[8] using the $I + O_3$ reaction to produce IO, and the results of Stickel *et al.*[4] using the $O + I_2$ reaction in the presence of O_3 indicate a significant pressure dependence in the measured rate constant. Measurements from this system can only provide values for the rate constants of non-I-atm-producing channels (i.e., $k_1 + 0.5k_3 + k_4[M]$). The low pressure intercept values of Clyne and Cruse,[7] Jenkin and Cox,[1] and Sander[2] are in good agreement when recalculated using the appropriate temperature-dependent cross sections of Sander: i.e., 2.2×10^{-11} cm^3 molecule^{-1} s^{-1} (298 K), 1.5×10^{-11} cm^3 molecule^{-1} s^{-1} (277 K) and 2.5×10^{-11} cm^3 molecule^{-1} s^{-1} (298 K), respectively, with $\sigma = 3.1\times10^{-17}$ cm^2 molecule^{-1} (298 K) and $\sigma = 4.0\times10^{-17}$ cm^2 molecule^{-1} (277 K). These values are probably measurements of $0.5k_3$ since Sander[2] found no evidence for I_2 production (i.e., $k_1 = 0$). At higher pressures, the results of Jenkin and Cox[1] and Cox and Coker[8] using molecular modulation are much greater than those of Sander[2] using flash photolysis, probably due to complications arising from the production of iodine oxide aerosols, which may lead to enhanced IO removal. The recent high-pressure result of Stickel *et al.*[4] is in much closer agreement with that of Sander.[2] This suggests that the value of $1\times10^{-30}[M]$ cm^3 molecule^{-1} s^{-1} at 298 K given by Sander is the best estimate of $k_4[M]$. Owing to the complex nature of this reaction, however, we prefer to make no firm recommendations concerning the relative importance of the various reaction channels until additional data are available.

References

[1] M. E. Jenkin and R. A. Cox, J. Phys. Chem. **89**, 192 (1985).
[2] S. P. Sander, J. Phys. Chem. **90**, 2194 (1986).
[3] D. Martin, J. L. Jourdain, G. Laverdet, and G. Le Bras, Int. J. Chem. Kinet. **19**, 503 (1987).
[4] R. E. Stickel, A. J. Hynes, J. D. Bradshaw, W. L. Chameides, and D. D. Davis, J. Phys. Chem. **92**, 1862 (1988).
[5] M. E. Jenkin, R. A. Cox, and D. E. Candeland, J. Atm. Chem. **2**, 359 (1985).
[6] CODATA Supplement I, 1982 (see References in Introduction).
[7] M. A. A. Clyne and H. W. Cruse, Trans. Faraday Soc. **66**, 2227 (1970).
[8] R. A. Cox and G. B. Coker, J. Phys. Chem. **87**, 4478 (1983).

$IO + NO_2 + M \rightarrow IONO_2 + M$

Comments

The data by Jenkin and Cox,[1] on which our earlier recommendation[2] was based, have since been published.

References

[1] M. E. Jenkin and R. A. Cox, J. Phys. Chem. **89**, 192 (1985).
[2] CODATA Supplement II, 1984 (see References in Introduction).

$IO + CH_3SCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.0 \pm 1.5)\times10^{-11}$	296	Barnes *et al.*, 1987[1]	(a)
$(1.5 \pm 0.5)\times10^{-11}$	298	Martin *et al.*, 1987[2]	(b)

Comments

(a) IO generated by steady state photolysis of NO_2 in excess I_2 at 760 Torr total pressure. k obtained from numerical simulation of the variation of product and reagent distributions with time. DMS, NO_2, NO, and DMSO measured using FTIR, and quantitative production of DMSO observed compared with DMS removed. IO + DMS reaction occurring in competition with IO + NO and IO + NO_2.

(b) Discharge flow–mass spectrometric technique at 1 Torr total pressure. IO generated from microwave discharge of O_2 in the presence of I_2. IO and DMS concentrations similar, so IO + DMS reaction occurring in competition with IO + IO. k concluded from consumption of DMS. DMSO observed as product.

Preferred Value

No recommendation.

Comments on Preferred Value

The results of the studies provide values for k that are in reasonable agreement. Both measurements, however, depend on values adopted for competing rate constants, and in the absence of data where IO is monitored directly, no firm recommendation is made.

References

[1] I. Barnes, K. H. Becker, P. Carlier, and G. Mouvier, Int. J. Chem. Kinet. **19**, 489 (1987).
[2] D. Martin, J. L. Jourdain, G. Laverdet, and G. Le Bras, Int. J. Chem. Kinet. **19**, 503 (1987).

$IO + h\nu \rightarrow$ products

Comments

Three new measurements of the absorption cross section at the band head of the $(v' = 4) \leftarrow (v'' = 0)$ band in the $A\,^2\pi \leftarrow X\,^2\pi$ system at 427 nm have been reported. Jenkin and Cox[1] used modulated photolysis of NO_2 to produce $O(^3P)$ with IO production from the $O + I_2$ reaction. They obtained $\sigma = (2.2 \pm 0.5) \times 10^{-17}$ cm^2 molecule^{-1} at 426.9 nm with a spectral bandwidth of 0.27 nm and a temperature of 306 K.

Sander[2] used flash photolysis of O_2–I_2 mixtures and measured IO absorption at 427.2 nm with a resolution of 0.17 nm. The cross sections measured at six temperatures in the range 250–373 K are given in the table.

Temperature dependence of the IO cross section at 427.2 nm

Temp./K	$10^{17}\sigma$/cm^2
250	5.3 ± 0.5
273	4.3 ± 0.4
298	3.1 ± 0.3
317	2.3 ± 0.2
341	2.3 ± 0.2
373	2.1 ± 0.2

A strong temperature dependence is apparent at $T < 317$ K, σ increasing with decreasing temperature. The difference in the quoted position of the band head in the study of Sander indicates a spectrometer calibration problem.

Stickel *et al.*[3] used laser flash photolysis of O_3 in the presence of I_2 and IO was measured by absorption on a beam from an eximer pumped dye laser with a bandwidth of 0.01 nm (fwhm) in a multipass arrangement. A value of $\sigma = (3.1 \pm 0.6) \times 10^{-17}$ cm^2 molecule^{-1} for the 4-0 band was obtained at room temperature. They also present a plot of absorption cross section versus wavelength for the (5,0), (4,0), (3,0), (2,0), and (1,0) bands. No absorption was found for the (0,0) band, in contrast to the earlier work of Cox and Coker,[4] on which the previous recommendation[5] was based.

There is now good agreement between the results of Sander[2] (at 298 K), Stickel *et al.*[3] and Cox and Coker[4] (who obtained $\sigma = (3.1^{+2.0}_{-1.5}) \times 10^{-17}$ cm^2 molecule^{-1}) for the cross section at the band head of the 4-0 band. The lower value of Jenkin and Cox[1] can only partly be accounted for by the temperature effect.

Stickel *et al.* point out an error in Table II of Ref. 4 where the listed σ values averaged over 5 nm are a factor of 10 higher than the true values based on the data plotted in Fig. 1 of that work. The atmospheric photolysis rate calculated from the tabulated data for a solar zenith angle of 40° (i.e., 0.3 s^{-1}) is consequently a factor of 10 too high. Stickel *et al.* do not present averaged cross-section data, so it is not possible to utilize their measurements over the whole spectral range.

The preferred values,[5] which are based on a value of $\sigma = 3.1 \times 10^{-17}$ cm^2 molecule^{-1} at the 4-0 band head and the (correct) averaged values from Ref. 4 remain unchanged.

References

[1] M. E. Jenkin and R. A. Cox, J. Phys. Chem. **89**, 192 (1985).
[2] S. P. Sander, J. Phys. Chem. **90**, 2194 (1986).
[3] R. E. Stickel, A. J. Hynes, J. D. Bradshaw, W. L. Chameides, and D. D. Davis, J. Phys. Chem. **92**, 1862 (1988).
[4] R. A. Cox and G. B. Coker, J. Phys. Chem. **87**, 4478 (1983).
[5] CODATA Supplement II, 1984 (see References in Introduction).

Appendix I

Enthalpy Data*

Substance	$\Delta H_f^\circ(298)$ kJ mol^{-1}	$\Delta H_f^\circ(0)$ kJ mol^{-1}	Notes
H	217.997	216.03	1
H_2	0	0	1
O	249.17	246.78	1
$O(^1D)$	438.9	436.6	2
O_2	0	0	1
$O_2(^1\Delta)$	94.3	94.3	2
$O_2(^1\Sigma)$	156.9	156.9	2
O_3	142.7	145.4	3
HO	39.3	39.0	4
HO_2	14.6		4
H_2O	– 241.81	– 238.92	1
H_2O_2	– 136.32	– 130.04	3
N	472.68	470.82	1
N_2	0	0	1
NH	343	343	2
NH_2	185.4	188.4	4
NH_3	– 45.94	– 38.95	1
NO	90.25	89.75	3
NO_2	33.2	36	3
NO_3	72.8		21
N_2O	82.05	85.50	3
N_2O_4	9.1	18.7	6
N_2O_5	11.3	23.8	3
HNO	99.6	102.5	6
HNO_2	– 79.5	– 74	3
HNO_3	– 135.06	– 125.27	3
HO_2NO_2	– 57		10
CH	596.35		4
$CH_2(^3B_1)$	392.5		4
$CH_2(^1A_1)$	430.1		4
CH_3	145.6	149	4,6
CH_4	– 74.81	– 66.82	3
CN	435		4,6
HCN	135		6
NCO	159		6
CO	– 110.53	– 113.81	1
CO_2	– 393.51	– 393.14	1
HCO	37.2		4
CH_2O	– 108.6	– 104.7	2
CH_3O	17.6		4
HCOOH	– 378.8	– 371.6	7
CH_3O_2	23.0		4
CH_2OH	– 25.9		4
CH_3OH	– 201.6		7
CH_3OOH	– 131		5
CH_3ONO	– 65.3		5
CH_3ONO_2	– 119.7		5
$CH_3O_2NO_2$	– 44		10
C_2H	565		4
C_2H_2	228.0		7
C_2H_3	276		4
C_2H_4	52.2		7
C_2H_5	117.0		4
C_2H_6	– 84.0		7
CH_2CN	244.8		4
CH_3CN	64.3		8
CH_2CO	– 59.54		7
CH_3CO	– 24.3		4
CH_3CHO	– 165.8		7,8
C_2H_5O	– 17.2		4
C_2H_5OH	– 234.8		7,8
$(CHO)_2$	– 211.9		7,8
CH_3CO_2	– 207.5		4
$C_2H_5O_2$	– 7.5		5
CH_3OOCH_3	– 125.7		7,8
$CH_2=CHCH_2$	163.6		4
C_3H_6	20.2		7,8

Enthalpy data—Continued

Substance	$\Delta H_f^\circ(298)$ kJ mol^{-1}	$\Delta H_f^\circ(0)$ kJ mol^{-1}	Notes
n-C_3H_7	95.4		4
i-C_3H_7	79.6		4
C_3H_8	– 104.5		7,8
C_2H_5CHO	– 187.4		7,8
CH_3COCH_3	– 217.2		7,8
CH_3COCHO	– 271.1		7,8
CH_3COCH_2	– 23.9		4
S	276.98	274.72	1
S_2	128.49	128.20	1
HS	140.6		4
H_2S	– 20.63	– 17.70	3
SO	5.0	5.0	6
SO_2	– 296.81	– 294.26	1
SO_3	– 395.7	– 390	3
HSO	– 4		23
HSO_2	– 222		25
$HOSO_2$	– 385		26
CS	272	268	9
CS_2	117.2	116.6	3
CH_3SCH_2	149		4
CH_3SCH_3	– 37.2		9
CH_3SSCH_3	– 24.3		9
OCS	– 142	– 142	3
F	79.39	77.28	1
F_2	0	0	1
HF	– 273.30	– 273.26	1
HOF	– 98	– 95	6
FO	109	109	5
FO_2	26.1		28
FONO	– 63.4		10
FNO_2	– 108.8		10
$FONO_2$	10	18	6
CF_2	– 194.1		4
CF_3	– 476.4		4
CF_4	– 933	– 927	11
FCO	– 170	– 170	6
COF_2	– 634.7	– 631.6	3
Cl	121.30	119.62	1
Cl_2	0	0	1
HCl	– 92.31	– 92.13	1
ClO	102	102	2,12
ClOO	95		15
OClO	101	104	27
sym-ClO_3	155		3
Cl_2O	81.4	83.2	13
Cl_2O_2	130		22
HOCl	– 78	– 75	2,14
ClNO	51.7	53.6	6
$ClNO_2$	12.5	18.0	3
ClONO	56		10
$ClONO_2$	26.4		13
FCl	– 50.7	– 50.8	6
CCl	441		4
CCl_2	239		4
CCl_3	79.5		4
CCl_4	– 95.8	– 93.6	16
$CHCl_3$	– 102.9	– 98.0	16
CH_2Cl	130.1		24
$CHCl_2$	107.5		4
CH_2Cl_2	– 95.4	– 88.5	16
CH_3Cl	– 82.0	– 74.0	16
ClCO	– 17		5
$COCl_2$	– 220.1	– 218.4	2
$CFCl_2$	– 96		4
$CFCl_3$	– 284.9	– 281.8	17
CF_2Cl	– 269.0		4
CF_2Cl_2	– 493.3	– 489.1	17

Enthalpy data—Continued

Substance	$\Delta H_f^\circ(298)$ kJ mol^{-1}	$\Delta H_f^\circ(0)$ kJ mol^{-1}	Notes
CF_3Cl	− 707.9	− 702.9	17
$CHFCl_2$	− 284.9	− 279.5	17
CHF_2Cl	− 483.7	− 477.4	17
COFCl	− 427	− 423	6
C_2Cl_4	− 12.4	− 11.9	6
C_2HCl_3	− 7.8	− 4.3	3
CH_3CCl_3	− 142.3	− 145.0	18
Br	111.86	117.90	1
$Br_2(g)$	30.91	45.69	1
HBr	− 36.38	− 28.54	1
HOBr	− 80		5
BrO	125	133	3
BrNO	82.2	91.5	3
$BrONO_2$	47		10
BrCl	14.6	22.1	6
CH_2Br	173.6		4
CH_3Br	− 37.7	− 22.3	19
I	106.762		1
$I_2(g)$	62.421		1
HI	26.36		1
IO	176		4
INO	121.3	124.3	20
INO_2	60.2	66.5	20

*Most of the thermochemical data have been taken from evaluations or from reviews. In some cases, we have selected more recent experimental data which appear to be reliable.

Notes

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Appendix II

Conversion Tables

Equivalent second order rate constants

A \ B	cm^3 mol^{-1} s^{-1}	dm^3 mol^{-1} s^{-1}	m^3 mol^{-1} s^{-1}	cm^3 $molecule^{-1}$ s^{-1}	$(mm\ Hg)^{-1}$ s^{-1}	atm^{-1} s^{-1}	ppm^{-1} min^{-1}	$m^2\ kN^{-1}\ s^{-1}$
1 $cm^3\ mol^{-1}\ s^{-1}$ =	1	10^{-3}	10^{-6}	1.66×10^{-24}	$1.604 \times 10^{-5} T^{-1}$	$1.219 \times 10^{-2} T^{-1}$	2.453×10^{-9}	$1.203 \times 10^{-4} T^{-1}$
1 $dm^3\ mol^{-1}\ s^{-1}$ =	10^3	1	10^{-3}	1.66×10^{-21}	$1.604 \times 10^{-2} T^{-1}$	$12.19 T^{-1}$	2.453×10^{-6}	$1.203 \times 10^{-1} T^{-1}$
1 $m^3\ mol^{-1}\ s^{-1}$ =	10^6	10^3	1	1.66×10^{-18}	$16.04 T^{-1}$	$1.219 \times 10^4 T^{-1}$	2.453×10^{-3}	$120.3 T^{-1}$
1 $cm^3\ molecule^{-1}\ s^{-1}$ =	6.023×10^{23}	6.023×10^{20}	6.023×10^{17}	1	$9.658 \times 10^{18} T^{-1}$	$7.34 \times 10^{21} T^{-1}$	1.478×10^{15}	$7.244 \times 10^{19} T^{-1}$
1 $(mm\ Hg)^{-1}\ s^{-1}$ =	$6.236 \times 10^4 T$	$62.36 T$	$6.236 \times 10^{-2} T$	$1.035 \times 10^{-19} T$	1	760	4.56×10^{-2}	7.500
1 $atm^{-1}\ s^{-1}$	$82.06 T$	$8.206 \times 10^{-2} T$	$8.206 \times 10^{-5} T$	$1.362 \times 10^{-22} T$	1.316×10^{-3}	1	6×10^{-5}	9.869×10^{-3}
1 $ppm^{-1}\ min^{-1}$ = at 298 K, 1 atm total pressure	4.077×10^8	4.077×10^5	407.7	6.76×10^{-16}	21.93	1.667×10^4	1	164.5
1 $m^2\ kN^{-1}\ s^{-1}$ =	$8314 T$	$8.314 T$	$8.314 \times 10^{-3} T$	$1.38 \times 10^{-20} T$	0.1333	101.325	6.079×10^{-3}	1

To convert a rate constant from one set of units A to a new set B find the conversion factor for the row A under column B and multiply the old value by it, e.g. to convert $cm^3\ molecule^{-1}\ s^{-1}$ to $m^3\ mol^{-1}\ s^{-1}$ multiply by 6.023×10^{17}.

Table adapted from High Temperature Reaction Rate Data No. 5, The University, Leeds (1970).

Equivalent third order rate constants

B / A	cm^6 mol^{-2} s^{-1}	dm^6 mol^{-2} s^{-1}	m^6 mol^{-2} s^{-1}	cm^6 $molecule^{-2}$ s^{-1}	$(mm\ Hg)^{-2}$ s^{-1}	atm^{-2} s^{-1}	ppm^{-2} min^{-1}	$m^4\ kN^{-2}\ s^{-1}$
1 $cm^6\ mol^{-2}\ s^{-1}$ =	1	10^{-6}	10^{-12}	2.76×10^{-48}	$2.57 \times 10^{-10} T^{-2}$	$1.48 \times 10^{-4} T^{-2}$	1.003×10^{-19}	$1.447 \times 10^{-8} T^{-2}$
1 $dm^6\ mol^{-2}\ s^{-1}$ =	10^6	1	10^{-6}	2.76×10^{-42}	$2.57 \times 10^{-4} T^{-2}$	$148 T^{-2}$	1.003×10^{-13}	$1.447 \times 10^{-2} T^{-2}$
1 $m^6\ mol^{-2}\ s^{-1}$ =	10^{12}	10^6	1	2.76×10^{-36}	$257 T^{-2}$	$1.48 \times 10^8 T^{-2}$	1.003×10^{-7}	$1.447 \times 10^4 T^{-2}$
1 $cm^6 molecule^{-2}\ s^{-1}$ =	3.628×10^{47}	3.628×10^{41}	3.628×10^{35}	1	$9.328 \times 10^{37} T^{-2}$	$5.388 \times 10^{43} T^{-2}$	3.64×10^{28}	$5.248 \times 10^{39} T^{-2}$
1 $(mm\ Hg)^{-2}\ s^{-1}$ =	$3.89 \times 10^9 T^2$	$3.89 \times 10^3 T^2$	$3.89 \times 10^{-3} T^2$	$1.07 \times 10^{-38} T^2$	1	5.776×10^5	3.46×10^{-5}	56.25
1 $atm^{-2}\ s^{-1}$ =	$6.733 \times 10^3 T^2$	$6.733 \times 10^{-3} T^2$	$6.733 \times 10^{-9} T^2$	$1.86 \times 10^{-44} T^2$	1.73×10^{-6}	1	6×10^{-11}	9.74×10^{-5}
1 $ppm^{-2}\ min^{-1}$ = at 298 K, 1 atm total pressure	9.97×10^{18}	9.97×10^{12}	9.97×10^6	2.75×10^{-29}	2.89×10^4	1.667×10^{10}	1	1.623×10^6
1 $m^4\ kN^{-2}\ s^{-1}$ =	$6.91 \times 10^7 T^2$	$69.1 T^2$	$6.91 \times 10^{-5} T^2$	$1.904 \times 10^{-40} T^2$	0.0178	1.027×10^4	6.16×10^{-7}	1

See note to table for second order rate constants.

Conversion factors for units of optical absorption coefficients

B / A	(Cross section σ) $cm^2\ molecule^{-1}$ base e	(atm at 273)$^{-1}$ cm^{-1} base e	$dm^3\ mol^{-1}\ cm^{-1}$ base 10	$cm^2\ mol^{-1}$ base 10
1 (atm at 298)$^{-1}$ cm^{-1} base e =	4.06×10^{-20}	1.09	10.6	1.06×10^4
1 (atm at 298)$^{-1}$ cm^{-1} base 10 =	9.35×10^{-20}	2.51	24.4	2.44×10^4
1 (mm Hg at 298)$^{-1}$ cm^{-1} base 10 =	7.11×10^{-17}	1.91×10^3	1.86×10^4	1.86×10^7
1 (atm at 273)$^{-1}$ cm^{-1} base e =	3.72×10^{-20}	1	9.73	9.73×10^3
1 (atm at 273)$^{-1}$ cm^{-1} base 10 =	8.57×10^{-20}	2.303	22.4	2.24×10^4
1 $dm^3\ mol^{-1}\ cm^{-1}$ base 10 =	3.82×10^{-21}	0.103	1	10^3
1 $cm^2\ mol^{-1}$ base 10 =	3.82×10^{-24}	1.03×10^{-4}	10^{-3}	1
1 $cm^2\ molecule^{-1}$ base e =	1	2.69×10^{19}	2.62×10^{20}	2.62×10^{23}

To convert an absorption coefficient from one set of units A to a new set B, multiply by the value tabulated for row A under column B, e.g. to convert the value of the absorption coefficient expressed in $dm^3\ mol^{-1}\ cm^{-1}$ base 10 to (atm at 273)$^{-1}$ cm^{-1} base e, multiply by 0.103.

Units for Expressing Pressure

In this evaluation we have expressed pressures in terms of Torr and atmosphere. These are defined in terms of SI units by the following equations:

1 Torr = 133.322 Pa

1 Atm = 101,325 Pa.