

**Evaluated kinetic and
photochemical data
for atmospheric
chemistry**

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Evaluated kinetic and photochemical data for atmospheric chemistry: Volume III – reactions of inorganic halogens

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Abstract

This article, the third in the series, presents kinetic and photochemical data evaluated by the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. It covers the gas phase and photochemical reactions of inorganic halogen species, which were last published in J. Phys. Chem. Ref. Data in 2000 (Atkinson et al., 2000), and were updated on the IUPAC website in 2003. The article consists of a summary sheet, containing the recommended kinetic parameters for the evaluated reactions, and five appendices containing the data sheets, which provide information upon which the recommendations are made.

1 Introduction

In the mid 1970s it was appreciated that there was a need for the establishment of an international panel to produce a set of critically evaluated rate parameters for reactions of interest for atmospheric chemistry. To this end the CODATA Task Group on Chemical Kinetics, under the auspices of the International Council of Scientific Unions (ICSU), was constituted in 1977 and tasked to produce an evaluation of relevant, available kinetic and photochemical data. The first evaluation by this international committee was published in J. Phys. Chem. Ref. Data in 1980 (Baulch et al., 1980), followed by Supplements in 1982 (Baulch et al., 1982) and 1984 (Baulch et al., 1984). In 1986 the IUPAC Subcommittee on Data Evaluation superseded the original CODATA Task Group for Atmospheric Chemistry, and the Subcommittee has continued its data evaluation program with Supplements published in 1989 (Atkinson et al., 1989), 1992 (Atkinson et al., 1992), 1997 (Atkinson et al., 1997a), 1997 (Atkinson et al., 1997b), 1999 (Atkinson et al., 1999) and 2000 (Atkinson et al., 2000). Following the last of these reports, Supplement VIII (Atkinson et al., 2000), the evaluation has continued to be updated and published on the worldwide web (<http://www.iupac-kinetic.ch.cam.ac.uk/>). The IUPAC website hosts an interactive data base with a search facility and implemented

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hyperlinks between the summary table and the data sheets, both of which can be downloaded as individual PDF files. In order to further enhance the accessibility of this updated material to the scientific community, the evaluation is being published as a series of articles in Atmospheric Chemistry and Physics. This article is the third of the series, Volume III.

2 Summary of recommended rate coefficients for inorganic reactions

The ordering of families in the Summary Table is: FO_x (Appendix 1), ClO_x (Appendix 2), BrO_x (Appendix 3) and IO_x (Appendix 4). Photochemical reactions are listed in Appendix 5. The reactions are numbered sequentially for the whole Volume. Within each family, reactions are listed in the order: $\text{O}(^3\text{P})$, $\text{O}(^1\text{D})$, halogen atom, OH radical, NO_3 radical and halogen oxide reactions. Chemical reactions are listed as first reactant (usually an atom or radical) + second reactant (usually a molecule). Each datasheet has a unique identifier: 'Volume: Appendix: reaction number'. For example, the first reaction in the summary sheet below refers to Datasheet 'III.A1.1'.

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3 Table 1. Summary of recommended rate coefficients for inorganic reactions

reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/K^a$
FO_x Reactions: based on data sheets in Appendix 1						
1	O + FO → O ₂ + F	2.7 × 10 ⁻¹¹	±0.3			
2	O + FO ₂ → O ₂ + FO	5 × 10 ⁻¹¹	±0.7			
3	O(¹ D) + HF → HO + F	1.5 × 10 ⁻¹¹	±0.1			
	→ O(³ P) + HF	3.6 × 10 ⁻¹¹	±0.1			
	overall	5.1 × 10 ⁻¹¹	±0.2			
4	F + H ₂ → HF + H	2.4 × 10 ⁻¹¹	±0.1	1.1 × 10 ⁻¹⁰ exp(-450/T)	190–380	±100
5	F + H ₂ O → HF + HO	1.4 × 10 ⁻¹¹	±0.1	1.4 × 10 ⁻¹¹	240–380	±200
6	F + O ₂ + M → FO ₂ + M	5.8 × 10 ⁻³³ [N ₂]	(k ₀) ±0.3	5.8 × 10 ⁻³³ (T/300) ^{-1.7} [N ₂]	100–380	Δn = ±0.5
		1.2 × 10 ⁻¹⁰	(k _∞) ±0.3	1.2 × 10 ⁻¹⁰	100–380	Δk _∞ = ±0.3
		F _c ≈ 0.5	F _c ≈ 0.5	100–380		
7	FO ₂ + M → F + O ₂ + M	1.5 × 10 ⁻¹⁷ [N ₂]	(k ₀ /s ⁻¹) ±0.3	8.4 × 10 ⁻⁹ (T/300) ^{-1.25} ×	310–420	±500
				exp(-5990/T)[N ₂]		Δn = ±0.5
		3.1 × 10 ⁵	(k _∞ /s ⁻¹) ±0.3	1.7 × 10 ¹⁴ (T/300) ^{0.45} ×	310–420	±500
		F _c ≈ 0.5	F _c ≈ 0.5	310–420	Δn = ±0.5	
8	F + O ₃ → FO + O ₂	1.0 × 10 ⁻¹¹	±0.25	2.2 × 10 ⁻¹¹ exp(-230/T)	250–370	±200
9	F + HONO ₂ → HF + NO ₃	2.3 × 10 ⁻¹¹	±0.1	6.0 × 10 ⁻¹² exp(400/T)	260–320	±200
10	FO + O ₃ → products	< 1 × 10 ⁻¹⁴				
11	FO + NO → F + NO ₂	2.2 × 10 ⁻¹¹	±0.15	8.2 × 10 ⁻¹² exp(300/T)	290–850	±200
12	FO + FO → products	1.0 × 10 ⁻¹¹	±0.2	1.0 × 10 ⁻¹¹	290–440	±250
13	FO ₂ + O ₃ → products	< 4 × 10 ⁻¹⁶				
14	FO ₂ + NO → FNO + O ₂	7.5 × 10 ⁻¹³	±0.3	7.5 × 10 ⁻¹² exp(-690/T)	190–300	±400
15	FO ₂ + NO ₂ → products	4.0 × 10 ⁻¹⁴	±0.3	3.8 × 10 ⁻¹¹ exp(-2040/T)	260–320	±500

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reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/K^a$
<i>CIO_x Reactions: based on data sheets in Appendix 2</i>						
16	O + HOCl → HO + ClO	1.7×10^{-13}	±0.5	1.7×10^{-13}	210–300	±300
17	O + ClO → Cl + O ₂	3.7×10^{-11}	±0.6	$2.5 \times 10^{-11} \exp(110/T)$	220–390	±50
18	O + OCIO → O ₂ + ClO	1.0×10^{-13}	±0.3	$2.4 \times 10^{-12} \exp(-960/T)$	240–400	±300
19	O + OCIO + M → ClO ₃ + M	$1.8 \times 10^{-31} [N_2]$	(k_0)	$1.8 \times 10^{-31} (T/298)^{-1} [N_2]$	240–320	$\Delta n = \pm 0.5$
		2.8×10^{-11}	(k_∞)	2.8×10^{-11}	240–320	$\Delta n = \pm 1$
		$F_c = 0.5$				
20	O + Cl ₂ O → ClO + ClO	4.5×10^{-12}	±0.15	$2.7 \times 10^{-11} \exp(-530/T)$	230–380	±200
21	O + ClONO ₂ → products	2.2×10^{-13}	±0.08	$4.5 \times 10^{-12} \exp(-900/T)$	200–330	±150
22	Cl + H ₂ → HCl + H	1.7×10^{-14}	±0.1	$3.9 \times 10^{-11} \exp(-2310/T)$	200–310	±200
23	Cl + HO ₂ → HCl + O ₂	3.4×10^{-11}	±0.2			
		9.3×10^{-12}	±0.2	$6.3 \times 10^{-11} \exp(-570/T)$	230–420	±200
	→ products	4.3×10^{-11}		4.3×10^{-11}	230–420	
24	Cl + H ₂ O ₂ → HCl + HO ₂	4.1×10^{-13}	±0.2	$1.1 \times 10^{-11} \exp(-980/T)$	260–430	±500
25	Cl + O ₂ + M → ClOO + M	$1.4 \times 10^{-33} [N_2]$	(k_0)	$1.4 \times 10^{-33} (T/300)^{-3.9} [N_2]$	160–300	$\Delta n = \pm 1$
		$1.6 \times 10^{-33} [O_2]$	(k_0)	$1.6 \times 10^{-33} (T/300)^{-2.9} [O_2]$	160–300	$\Delta n = \pm 1$
26	ClOO + M → Cl + O ₂ + M	$6.2 \times 10^{-13} [N_2]$	(k_0/s^{-1})	$2.8 \times 10^{-10} \exp(-1820/T) [N_2]$	160–300	±200
27	Cl + CO + M → ClCO + M	$1.3 \times 10^{-33} [N_2]$	(k_0)	$1.3 \times 10^{-33} (T/300)^{-3.8} [N_2]$	180–300	$\Delta n = \pm 1$
28	ClCO + M → Cl + CO + M	$2.0 \times 10^{-14} [N_2]$	(k_0/s^{-1})	$4.1 \times 10^{-10} \exp(-2960/T) [N_2]$	180–300	±200
29	Cl + O ₃ → ClO + O ₂	1.2×10^{-11}	±0.06	$2.8 \times 10^{-11} \exp(-250/T)$	180–300	$^{+100}$ $_{-150}$
30	Cl + HONO ₂ → HCl + NO ₃	$< 2 \times 10^{-16}$				
31	Cl + NO ₃ → ClO + NO ₂	2.4×10^{-11}	±0.2	2.4×10^{-11}	200–300	±400
32	Cl + OCIO → ClO + ClO	5.7×10^{-11}	±0.1	$3.2 \times 10^{-11} \exp(170/T)$	220–430	±200
33	Cl + Cl ₂ O → Cl ₂ + ClO	9.6×10^{-11}	±0.1	$6.2 \times 10^{-11} \exp(130/T)$	230–380	±130
34	Cl + Cl ₂ O ₂ → Cl ₂ + ClOO	1.0×10^{-10}	±0.3	1.0×10^{-10}	230–300	±300
35	Cl + ClONO ₂ → Cl ₂ + NO ₃	1.0×10^{-11}	±0.1	$6.2 \times 10^{-12} \exp(145/T)$	190–360	±50

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reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/\text{K}^a$
36	HO + Cl ₂ → HOCl + Cl	6.5×10^{-14}	±0.08	$3.6 \times 10^{-12} \exp(-1200/T)$	230–360	±300
37	HO + HCl → H ₂ O + Cl	8.0×10^{-13}	±0.06	$1.8 \times 10^{-12} \exp(-240/T)$	200–300	±100
38	HO + HOCl → ClO + H ₂ O	5.0×10^{-13}	±0.5			
39	HO + ClO → HO ₂ + Cl	1.9×10^{-11}				
	→ HCl + O ₂	1.2×10^{-12}				
	overall	2.0×10^{-11}	±0.15	$7.3 \times 10^{-12} \exp(300/T)$	200–380	±100
40	HO + OCIO → HOCl + O ₂	6.6×10^{-12}	±0.3	$4.5 \times 10^{-13} \exp(800/T)$	290–480	±200
41	HO + ClNO ₂ → HOCl + NO ₂	3.6×10^{-14}	±0.3	$2.4 \times 10^{-12} \exp(-1250/T)$	260–350	±300
42	HO + ClONO ₂ → products	4.0×10^{-13}	±0.2	$1.2 \times 10^{-12} \exp(-330/T)$	240–390	±200
43	NO ₃ + HCl → HNO ₃ + Cl	$< 5 \times 10^{-17}$				
44	ClO + HO ₂ → HOCl + O ₂					
	→ HCl + O ₃					
	overall	6.9×10^{-12}	±0.20	$2.2 \times 10^{-12} \exp(340/T)$	230–300	±350
45	ClO + O ₃ → ClOO + O ₂	$< 1.5 \times 10^{-17}$				
	→ OCIO + O ₂	$< 1 \times 10^{-18}$				
46	ClO + NO → Cl + NO ₂	1.7×10^{-11}	±0.1	$6.2 \times 10^{-12} \exp(295/T)$	200–420	±100

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reaction number	Reaction	k_{298} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/K^a$
47	$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$	$1.6 \times 10^{-31}[\text{N}_2]$	(k_0)	± 0.1	$1.6 \times 10^{-31}(T/300)^{-3.4}[\text{N}_2]$	250–350 $\Delta n = \pm 1$
		7.0×10^{-11}	(k_∞)	± 0.3	7.0×10^{-11}	250–350 $\Delta \log k = \pm 0.3$
		$F_c = 0.5$			$F_c = \exp(-T/430)$	250–350
48	$\text{ClO} + \text{NO}_3 \rightarrow \text{ClOO} + \text{NO}_2$ $\rightarrow \text{OCIO} + \text{NO}_2$	1.2×10^{-13}		± 0.3		
		overall 4.6×10^{-13}		± 0.2	4.6×10^{-13}	210–360 ± 400
49	$\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$ $\rightarrow \text{Cl} + \text{ClOO}$ $\rightarrow \text{Cl} + \text{OCIO}$	4.8×10^{-15}		± 0.2	$1.0 \times 10^{-12} \exp(-1590/T)$	260–390 ± 300
		8.0×10^{-15}		± 0.2	$3.0 \times 10^{-11} \exp(-2450/T)$	260–390 ± 500
		3.5×10^{-15}		± 0.2	$3.5 \times 10^{-13} \exp(-1370/T)$	260–390 ± 300
50	$\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$	$2.0 \times 10^{-32}[\text{N}_2]$	(k_0)	± 0.1	$2.0 \times 10^{-32}(T/300)^{-4}[\text{N}_2]$	190–390 $\Delta n = \pm 1.5$
		1.0×10^{-11}	(k_∞)	± 0.3	1.0×10^{-11}	190–390 $\Delta \log k = \pm 0.3$
		$F_c = 0.45$			$F_c = 0.45$	190–390
51	$\text{Cl}_2\text{O}_2 + \text{M} \rightarrow \text{ClO} + \text{ClO} + \text{M}$	$2.3 \times 10^{-18}[\text{N}_2]$	(k_0/s^{-1})	± 0.3	$3.7 \times 10^{-7} \exp(-7690/T)[\text{N}_2](\text{s}^{-1})$	260–310 ± 900
		1.1×10^3	(k_∞/s^{-1})	± 0.3	$1.8 \times 10^{14} \exp(-7690/T)(k_0/\text{s}^{-1})$	260–310 ± 500
		$F_c = 0.45$			$F_c = 0.45$	260–310
52	$\text{ClO} + \text{OCIO} + \text{M} \rightarrow \text{Cl}_2\text{O}_3 + \text{M}$	$6.2 \times 10^{-32}[\text{N}_2]$	(k_0)	± 0.3	$6.2 \times 10^{-32}(T/300)^{-4.7}[\text{N}_2]$	200–300 $\Delta n = \pm 1$
		2.4×10^{-11}	(k_∞)	± 0.3	2.4×10^{-11}	200–300 $\Delta \log k_\infty = \pm 0.3$
		$F_c = 0.6$			$F_c = 0.6$	200–300
53	$\text{Cl}_2\text{O}_3 + \text{M} \rightarrow \text{ClO} + \text{OCIO} + \text{M}$	$4.1 \times 10^{-16}[\text{N}_2]$	(k_0/s^{-1})	± 0.5	$1.4 \times 10^{-10} \exp(-3810/T)[\text{N}_2]$	200–300 ± 500
		1.6×10^5	(k_∞/s^{-1})	± 0.5	$2.5 \times 10^{12} \exp(-4940/T)$	200–300 ± 500
54	$\text{OCIO} + \text{O}_3 \rightarrow \text{ClO}_3 + \text{O}_2$	3.0×10^{-19}		± 0.4	$2.1 \times 10^{-12} \exp(-4700/T)$	260–300 ± 1000
55	$\text{OCIO} + \text{NO} \rightarrow \text{NO}_2 + \text{ClO}$	3.6×10^{-13}		± 0.15	$1.1 \times 10^{-13} \exp(350/T)$	220–370 ± 200
56	$\text{OCIO} + \text{NO}_3 + \text{M} \rightarrow \text{products}$	see datasheet				
57	$\text{Cl}_2\text{O}_2 + \text{O}_3 \rightarrow \text{ClO} + \text{ClOO} + \text{O}_2$	$< 1 \times 10^{-19}$	(200 K)			

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BrO_x Reactions: based on data sheets in Appendix 3						
58	O + HOBr → HO + BrO	2.8×10^{-11}	±0.2	$1.2 \times 10^{-10} \exp(-430/T)$	230–430	± 300
59	O + BrO → HO + BrO	4.1×10^{-11}	±0.2	$1.9 \times 10^{-11} \exp(230/T)$	230–330	±150
60	Br + HO ₂ → HBr + O ₂	1.7×10^{-12}	±0.2	$7.7 \times 10^{-12} \exp(-450/T)$	230–390	±200
61	Br + H ₂ O ₂ → HBr + HO ₂ → HOBr + HO					
	Overall	$< 5 \times 10^{-16}$				
62	Br + O ₃ → BrO + O ₂	1.2×10^{-12}	±0.08	$1.7 \times 10^{-11} \exp(-800/T)$	190–430	±200
63	Br + NO ₂ + M → BrNO ₂ + M	$4.2 \times 10^{-31} [N_2]$ 2.7×10^{-11} $F_c = 0.55$	(k_0) ±0.3 (k_∞) ±0.4	$4.2 \times 10^{-31} (T/300)^{-2.4} [N_2]$ 2.7×10^{-11}	250–350 250–350	$\Delta n = \pm 1$ $\Delta \log k = \pm 0.4$
64	Br + OCIO → BrO + ClO	3.5×10^{-13}	±0.3	$2.7 \times 10^{-11} \exp(-1300/T)$	260–430	±300
65	Br + Cl ₂ O → BrCl + ClO	4.3×10^{-12}	±0.1	$2.1 \times 10^{-11} \exp(-470/T)$	220–410	±200
66	Br + Cl ₂ O ₂ → BrCl + ClOO	3.0×10^{-12}	±0.3			
67	HO + HBr → H ₂ O + Br	1.1×10^{-11}	±0.1	$5.5 \times 10^{-12} \exp(205/T)$	180–360	±250
68	HO + Br ₂ → HOBr + Br	4.5×10^{-11}	±0.1	$2.0 \times 10^{-11} \exp(240/T)$	230–360	±150
69	HO + BrO → products	4.1×10^{-11}	±0.3	$1.8 \times 10^{-11} \exp(250/T)$	230–350	±300
70	Br + NO ₃ → BrO + NO ₂	1.6×10^{-11}	±0.3			
71	BrO + NO ₃ → BrOO + NO ₂	1.0×10^{-12}	±0.5			
72	NO ₃ + HBr → HNO ₃ + Br	$< 1 \times 10^{-16}$				
73	BrO + HO ₂ → HOBr + O ₂ → HBr + O ₃					
	Overall	2.4×10^{-11}	±0.3	$4.5 \times 10^{-12} \exp(500/T)$	210–360	±200

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74	BrO + O ₃ → products	< 2 × 10 ⁻¹⁷					
75	BrO + NO → Br + NO ₂	2.1 × 10 ⁻¹¹	±0.1	8.7 × 10 ⁻¹² exp(260/T)	220–430	±100	
76	BrO + NO ₂ + M → BrONO ₂ + M	4.7 × 10 ⁻³¹ [N ₂]	(k ₀) ±0.1	4.7 × 10 ⁻³¹ (T/300) ^{-3.1} [N ₂]	240–350	Δn = ±1	
		1.8 × 10 ⁻¹¹	(k _∞) ±0.1	1.8 × 10 ⁻¹¹	240–350	Δn = ±1	
		F _c = 0.4		F _c = exp(-T/327)	240–350		
77	BrO + ClO → Br + ClOO	6.8 × 10 ⁻¹²	±0.1	1.6 × 10 ⁻¹² exp(430/T)	220–400	±200	
		→ Br + ClOO	6.1 × 10 ⁻¹²	±0.1	2.9 × 10 ⁻¹² exp(220/T)	220–400	±200
		→ BrCl + O ₂	1.0 × 10 ⁻¹²	±0.1	5.8 × 10 ⁻¹³ exp(170/T)	220–400	±200
78	BrO + BrO → 2Br + O ₂	2.7 × 10 ⁻¹²	±0.1	2.7 × 10 ⁻¹²	250–390	±200	
		→ Br ₂ + O ₂	4.8 × 10 ⁻¹³	±0.1	2.9 × 10 ⁻¹⁴ exp(840/T)	250–390	±200

IO_x Reactions: based on data sheets in Appendix 4

79	O + I ₂ → IO + I	1.25 × 10 ⁻¹⁰	±0.1			
80	O + IO → O ₂ + I	1.4 × 10 ⁻¹⁰	±0.2			
81	I + HO ₂ → HI + O ₂	3.8 × 10 ⁻¹³	±0.3	1.5 × 10 ⁻¹¹ exp(-1090/T)	280–360	±500
82	I + O ₃ → IO + O ₂	1.3 × 10 ⁻¹²	±0.05	2.1 × 10 ⁻¹¹ exp(-830/T)	230–370	±150
83	I + NO + M → INO + M	1.8 × 10 ⁻³² [N ₂]	(k ₀) ±0.1	1.8 × 10 ⁻³² (T/300) ^{-1.0} [N ₂]	290–450	Δn = ±0.5
		1.7 × 10 ⁻¹¹	(k _∞) ±0.5	1.7 × 10 ⁻¹¹	300–400	Δlogk = ±0.5
		F _c = 0.6		F _c = 0.6		

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reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/K^a$
84	I + NO ₂ + M → IONO ₂ + M	$3.0 \times 10^{-31}[\text{N}_2]$ 6.6×10^{-11} $F_c = 0.63$	$(k_0) \pm 0.2$ $(k_\infty) \pm 0.3$	$3.0 \times 10^{-31}(T/300)^{-1.0}[\text{N}_2]$ 6.6×10^{-11} $F_c = 0.63$		$\Delta n = \pm 1$ $\Delta \log k = \pm 0.3$
85	I + NO ₃ → IO + NO ₂	No recommendation				
86	I ₂ + NO ₃ → I + IONO ₂	No recommendation				
87	HO + HI → H ₂ O + I	7.0×10^{-11}	± 0.3	$1.6 \times 10^{-11} \exp(440/T)$	240–360	± 400
88	HO + I ₂ → HOI + I	2.1×10^{-10}	± 0.15	2.1×10^{-10}	240–350	± 300
89	NO ₃ + HI → HNO ₃ + I	No recommendation				
90	IO + HO ₂ → HOI + O ₂	8.4×10^{-11}	± 0.2	$1.4 \times 10^{-11} \exp(540/T)$	270–380	± 300
91	IO + O ₃ → I + 2O ₂ → OIO + O ₂	$< 1.0 \times 10^{-15}$ $< 2.0 \times 10^{-16}$				
92	IO + ClO → ICl + O ₂ → Cl + I + O ₂ → I + OCIO	2.4×10^{-12} 3.0×10^{-12} 6.6×10^{-12}				
	overall	1.2×10^{-11}	± 0.1	$4.7 \times 10^{-12} \exp(280/T)$	200–370	± 100
93	IO + BrO → Br + OIO overall	6.8×10^{-11} 8.5×10^{-11}	± 0.1	$1.5 \times 10^{-11} \exp(510/T)$	200–390	± 350
94	IO + IO → I + OIO overall	3.8×10^{-11} (1 bar) 9.9×10^{-11}	± 0.1	$5.4 \times 10^{-11} \exp(180/T)$	250–320	± 200
95	IO + NO → I + NO ₂	1.95×10^{-11}	± 0.15	$7.15 \times 10^{-12} \exp(300/T)$	240–370	± 100
96	IO + NO ₂ + M → IONO ₂ + M	$7.7 \times 10^{-31}[\text{N}_2]$ 1.6×10^{-11} $F_c = 0.4$	$(k_0) \pm 0.3$ $(k_\infty) \pm 0.3$	$7.7 \times 10^{-31}(T/300)^{-5}[\text{N}_2]$ 1.6×10^{-11}		$\Delta n = \pm 2$ $\Delta \log k = \pm 0.3$
97	IONO ₂ + M → products	2.9×10^{-3} (1 bar)	$(k/s^{-1}) \pm 1.0$	$1.1 \times 10^{-15} \exp(-12060/T)$	240–305	± 500
98	INO + INO → I ₂ + 2NO	1.3×10^{-14}	± 0.4	$8.4 \times 10^{-11} \exp(-2620/T)$	300–450	± 600
99	INO ₂ + INO ₂ → I ₂ + 2NO ₂	1.7×10^{-15}	± 0.7	$4.7 \times 10^{-13} \exp(-1670/T)$	270–350	± 1000
100	OIO + NO → IO + NO ₂	6.7×10^{-12}	± 0.3	$1.1 \times 10^{-12} \exp(542/T)$	240–320	± 250

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reaction number	Reaction	k_{298} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/\text{K}^a$
-----------------	----------	---	-------------------------	---	---------------	--------------------------

Photochemical Reactions: based on data sheets in Appendix 5

101	HCl + $h\nu$ → products
102	HOCl + $h\nu$ → products
103	OCIO + $h\nu$ → products
104	Cl ₂ O + $h\nu$ → products
105	Cl ₂ O ₂ + $h\nu$ → products
106	Cl ₂ O ₃ + $h\nu$ → products
107	CINO + $h\nu$ → products
108	CIONO + $h\nu$ → products
109	CINO ₂ + $h\nu$ → products
110	CIONO ₂ + $h\nu$ → products
111	Cl ₂ + $h\nu$ → products
112	HBr + $h\nu$ → products
113	HOBr + $h\nu$ → products
114	BrO + $h\nu$ → products
115	OBRO + $h\nu$ → products
116	BrONO ₂ + $h\nu$ → products
117	BrCl + $h\nu$ → products
118	Br ₂ + $h\nu$ → products
119	HI + $h\nu$ → products
120	HOI + $h\nu$ → products
121	IO + $h\nu$ → products
122	OIO + $h\nu$ → products
123	ICl + $h\nu$ → products
124	IBr + $h\nu$ → products
125	I ₂ + $h\nu$ → I + I

^aThe cited uncertainty is an expanded uncertainty corresponding approximately to a 95% confidence limit.

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4 Guide to the data sheets

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

4.1 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 the Thermodynamics Data summary.

The available kinetic data on the reactions are summarized under two headings: (i) Absolute Rate Coefficients, and (ii) Relative Rate Coefficients. Under these headings, we include new data which have been published since the last published IUPAC evaluation as well as the data used in deriving the preferred values. Under both of the headings above, the data are presented as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in a temperature dependent form over a stated temperature range. For bimolecular reactions, the temperature dependence is usually expressed in the normal Arrhenius form, $k = A \exp(-B/T)$, where $B = E/R$. For a few bimolecular reactions, we have listed temperature dependences in the alternative form, $k = A'T^{-n}$ or $CT^n \exp(-D/T)$, where the original authors have found this to give a better fit to the data. For pressure dependent combination and dissociation reactions, the non-Arrhenius temperature dependence is used. This is discussed more fully in a subsequent section of this Introduction.

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

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supplemented by a series of comments summarizing the experimental details. The following list of abbreviations, relating to experimental techniques, is used in the Techniques and Comments sections:

A – absorption

AS – absorption spectroscopy

CCD – charge coupled detector

CIMS – chemical ionization mass spectroscopy/spectrometric

CL – chemiluminescence

CRDS – cavity ring-down spectroscopy

DF – discharge flow

EPR – electron paramagnetic resonance

F – flow system

FP – flash photolysis

FTIR – Fourier transform infrared

FTS – Fourier transform spectroscopy

GC – gas chromatography/gas chromatographic

HPLC – high-performance liquid chromatography

IR – infrared

LIF – laser induced fluorescence

LMR – laser magnetic resonance

LP – laser photolysis

MM – molecular modulation

MS – mass spectrometry/mass spectrometric

P – steady state photolysis

PLP – pulsed laser photolysis

PR – pulse radiolysis

RA – resonance absorption

RF – resonance fluorescence

RR – relative rate

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S – static system
TDLS – tunable diode laser spectroscopy
UV – ultraviolet
UVA – ultraviolet absorption
5 VUVA – vacuum ultraviolet absorption

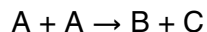
For measurements of relative rate coefficients, wherever possible the comments contain the actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient given in the table may be different
10 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)
15 in temperature dependent form over a stated temperature range. This is followed by a statement of the uncertainty limits in $\log k$ at 298 K and the uncertainty limits either in (E/R) or in n , for the mean temperature in the range. Some comments on the assignment of uncertainties are given later in this Introduction.

The “Comments on Preferred Values” describe how the selection was made and
20 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.

4.2 Conventions concerning rate coefficients

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



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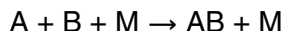
$$-\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A]^2.$$

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 righthand side.

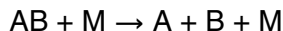
Representations of k as a function of temperature characterize simple “direct” bimolecular reactions. Sometimes it is found that k also depends on the pressure and the nature of the bath gas. This may be an indication of complex formation during the course of the bimolecular reaction, which is always the case in combination reactions. In the following sections the representations of k which are adopted in these cases are explained.

4.3 Treatment of combination and dissociation reactions

Unlike simple bimolecular reactions such as those considered in Sect. 1.2, combination reactions



and the reverse dissociation reactions



are composed of sequences of different types of physical and chemical elementary processes. Their rate coefficients reflect the more complicated sequential mechanism and depend on the temperature, T , and the nature and concentration of the third body, [M]. In this evaluation, the combination reactions are described by a formal second order rate law:

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

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while dissociation reactions are described by a formal first-order rate law:

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

In both cases, k depends on the temperature and on $[M]$.

5 In order to rationalize the representations of the rate coefficients used in this evaluation, we first consider the Lindemann-Hinshelwood reaction scheme. The combination reactions follow an elementary mechanism of the form,



10 while the dissociation reactions are characterized by:



15 Assuming quasi-stationary concentrations for the highly excited unstable species AB^* (i.e. that $d[AB^*]/dt \sim 0$), it follows that the rate coefficient for the combination reaction is given by:

$$k = k_1 \left(\frac{k_2[M]}{k_{-1} + k_2[M]} \right)$$

while that for the dissociation reaction is given by:

$$k = k_{-2}[M] \left(\frac{k_{-1}}{k_{-1} + k_2[M]} \right)$$

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In these equations the expressions before the parentheses represent the rate coefficients of the process initiating the reaction, whereas the expressions within the parentheses denote the fraction of reaction events which, after initiation, complete the reaction to products.

5 In the low pressure limit ($[M] \rightarrow 0$) the rate coefficients are proportional to $[M]$; in the high pressure limit ($[M] \rightarrow \infty$) they are independent of $[M]$. It is useful to express k in terms of the limiting low pressure and high pressure rate coefficients,

$$k_0 = \lim_{[M] \rightarrow 0} k([M]) \quad \text{and,} \quad k_\infty = \lim_{[M] \rightarrow \infty} k([M])$$

respectively. From this convention, the Lindemann-Hinshelwood equation is obtained

$$10 \quad k = \frac{k_0 k_\infty}{k_0 + k_\infty}$$

It follows that for combination reactions, $k_0 = k_1 k_2 [M] / k_{-1}$ and $k_\infty = k_1$, while for dissociation reactions, $k_0 = k_{-2} [M]$ and $k_\infty = k_{-1} k_{-2} / k_2$. Since detailed balancing applies, the ratio of the rate coefficients for combination and dissociation at a fixed T and $[M]$ is given by the equilibrium constant $K_c = k_1 k_2 / k_{-1} k_{-2}$.

15 Starting from the high-pressure limit, the rate coefficients fall-off with decreasing third body concentration $[M]$ and the corresponding representation of k as a function of $[M]$ is termed the “falloff curve” of the reaction. In practice, the above Lindemann-Hinshelwood expressions do not suffice to characterize the falloff curves completely. Because of the multistep character of the collisional deactivation ($k_2[M]$) and activation ($k_{-2}[M]$) processes, and energy- and angular momentum-dependencies of the association (k_1) and dissociation (k_{-1}) steps, as well as other phenomena, the falloff expressions have to be modified. This can be done by including a broadening factor F to the Lindemann-Hinshelwood expression (Troe, 1979):

$$20 \quad k = \frac{k_0 k_\infty}{k_0 + k_\infty} F = k_0 \left(\frac{1}{1 + \frac{k_0}{k_\infty}} \right) F = k_\infty \left(\frac{\frac{k_0}{k_\infty}}{1 + \frac{k_0}{k_\infty}} \right) F$$

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The broadening factor F depends on the ratio k_0/k_∞ , which is proportional to $[M]$, and can be used as a measure of “reduced pressure”. The first factors on the right-hand side represent the Lindemann-Hinshelwood expression and the additional broadening factor F , at not too high temperatures, is approximately given by (Troe, 1979):

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

where $\log = \log_{10}$ and $N = [0.75 - 1.27 \log F_c]$. In this way the three quantities k_0 , k_∞ , and F_c characterise the falloff curve for the present application.

The given approximate expression for the broadening factor F was obtained from statistical unimolecular rate theory in its simplest form (Troe, 1979). More rigorous representations require detailed information on the potential energy surfaces and on the collisional energy transfer step of the reaction. If this information is not available, one may assume typical behaviour and rely on the theoretical analysis given by Cobos and Troe (2003). For $T = 200\text{--}300$ K and the collider $M = N_2$ (with a collision efficiency $\beta_c \approx 0.3$), this treatment predicts $F_c \approx 0.49, 0.44, 0.39$, and 0.35 , if the reactants A and B in total have $r = 3, 4, 5$, or 6 rotational degrees of freedom, respectively (e.g. for the reaction $\text{HO} + \text{NO}_2$, one would have $r = 5$ and hence $F_c \approx 0.39$). It is also predicted that F_c , for the present applications, should be nearly temperature independent. Finally, more rigorous expressions for the broadening factors F are given in Cobos and Troe (2003) which, in general do not differ from the above formula by more than about 10 percent. Since the special properties of each reaction system may lead to some deviations from the given values of F_c , these should only be used for a first orientation. Larger deviations of experimentally fitted F_c -values from the given “standard values”, however, may be an indication for inadequate falloff extrapolations to k_0 and k_∞ . In this case, the apparent values for F_c , k_0 , and k_∞ obtained by fitting still can provide a satisfactory representation of the considered experimental data, in spite of the fact that inadequate values of k_0 and k_∞ are obtained by extrapolation.

If a given falloff curve is fitted in different ways, changes in F_c require changes in the limiting k_0 and k_∞ values. For the purpose of this evaluation, this is irrelevant if

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the preferred k_0 and k_∞ are used consistently together with the preferred F_c values. If the selected F_c value is too large, the values of k_0 and k_∞ obtained by fitting the falloff expression to the experimental data are underestimated. If F_c is too small, k_0 and k_∞ are overestimated. However uncertainties in F_c influence the fitted k_0 and k_∞ in different ways. A simpler policy of fitting falloff was chosen by the NASA/JPL panel (Sander et al., 2003) in putting $F=0.6$ and $N=1$. This generally leads to different values of the fitted k_0 and k_∞ and their temperature dependencies than derived here, although experimental data over the range of atmospheric interest can generally be reproduced equally well. However the derived k_0 and k_∞ may differ from the true limiting rate coefficients and thus should be interpreted by theory only with caution.

In the present evaluation, we generally follow the experimentally fitted values for F_c , k_0 , and k_∞ , provided F_c does not differ too much from the values given above. If large deviations are encountered, the experimental data are re-evaluated using the given F_c -values given above.

Besides the energy-transfer mechanism, i.e. Reactions (1), (-1), and (2), a second mechanism appears to be relevant for some reactions considered here. This is the radical-complex (or chaperon) mechanism



which, in the low pressure range, leads to

$$k_0 = (k_3/k_{-3})k_4[M].$$

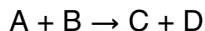
For some tri- and tetra-atomic adducts AB, this value of k_0 may exceed that from the energy-transfer mechanism and show stronger temperature dependencies. This mechanism may also influence high pressure experiments when k_0 from the radical-complex mechanism exceeds k_∞ from the energy-transfer mechanism (Oum et al., 2003). In

this case falloff over wide pressure ranges cannot be represented by contributions from the energy-transfer mechanism alone, in particular when measurements at pressures above about 10 bar are taken into consideration.

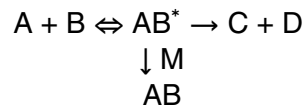
The dependence of k_0 and k_∞ on the temperature T is represented in the form $k \propto T^{-n}$ except for cases with an established energy barrier in the potential. We have used this form of temperature dependence because it usually gives a better fit to the data over a wider range of temperature than does the Arrhenius expression. It should be emphasised that the chosen form of the temperature dependence is often only adequate over limited temperature ranges such as 200–300 K. Obviously, the relevant values of n are different for k_0 and k_∞ . In this evaluation, values of k_0 are given for selected examples of third bodies M, and if possible for M=N₂, O₂ or air.

4.4 Treatment of complex-forming bimolecular reactions

Bimolecular reactions may follow the “direct” pathway



and/or involve complex formation,



We designate the rate coefficients of the individual steps as in Sect. 1.3, above:



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Assuming quasi-stationary concentrations of AB^* (i.e. $d[AB^*]/dt \sim 0$), a Lindemann-Hinshelwood type of analysis leads to,

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

$$\frac{d[C]}{dt} = k_D[A][B]$$

$$5 \quad \frac{d[A]}{dt} = (k_S + k_D)[A][B]$$

where

$$k_S = k_1 \left(\frac{k_2}{k_{-1} + k_2 + k_3} \right)$$

$$k_D = k_1 \left(\frac{k_3}{k_{-1} + k_2 + k_3} \right)$$

10 Note that since k_2 is proportional to $[M]$, k_S and k_D are dependent on the nature and concentration of the third body M , in addition to their temperature dependence. In reality, as for the combination and dissociation reactions, the given expressions for k_S and k_D have to be extended by suitable broadening factors F in order to account for the multistep character of process (2) and the energy dependencies of processes (1), (-1) and (3). These broadening factors, however, differ from those for combination and
 15 dissociation reactions. For simplicity, they are ignored in this evaluation such that k_D at high pressure approaches

$$k_D \rightarrow k_1 k_3 / k_2$$

which is inversely proportional to $[M]$. k_D may also be expressed by

$$k_D \approx k_{D0} k_S / k_{S0}$$

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where k_{D0} and k_{S0} are the respective limiting low-pressure rate coefficients for the formation of C+D or A+B at the considered [M]. When it is established that complex-formation is involved, this equation is used to characterize the increasing suppression of C+D formation with increasing [M].

5 4.5 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 the Thermodynamic Data summary. Calculated threshold wavelengths corresponding to these enthalpy changes are also listed, bearing in mind that the values calculated from the enthalpy changes at 298 K are not true “threshold values”.

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

The next table lists the preferred absorption cross-section data and the preferred quantum yields at appropriate wavelength intervals. For absorption cross-sections the intervals are usually 1 nm, 5 nm or 10 nm. Any temperature dependence of the absorption cross-sections is also given where possible. The aim in presenting these preferred data is to provide a basis for calculating atmospheric photolysis rates. For absorption continua the temperature dependence is often represented by Sulzer-Wieland type expressions (Astholz et al., 1981). Alternately a simple empirical expression of the form: $\log_{10}(\sigma_{T_1}/\sigma_{T_2})=B(T_1-T_2)$ is used.

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

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4.6 Conventions concerning absorption cross-sections

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

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

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

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

4.7 Assignment of uncertainties

Under the heading “reliability,” estimates have been made of the absolute accuracies of the preferred values of k at 298 K and of the preferred values of E/R over the quoted temperature range. The accuracy of the preferred rate coefficient at 298 K is quoted as the term $\Delta \log k$, where $\Delta \log k = D$ and D is defined by the equation, $\log_{10} k = C \pm D$. This is equivalent to the statement that k is uncertain to a factor of F , where $D = \log_{10} F$. The accuracy of the preferred value of E/R is quoted as the term $\Delta(E/R)$, where $\Delta(E/R) = G$ and G is defined by the equation $E/R = H \pm G$. D and G are expanded uncertainties corresponding approximately to a 95% confidence limit.

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

$$\Delta \log k(T) = \Delta \log k(298 \text{ K}) + 0.4343\{\Delta E/R(1/T - 1/298)\}$$

5 The assignment of these absolute uncertainties in k and E/R is a subjective assessment of the evaluators. They are not determined by a rigorous, statistical analysis of the database, which is generally too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the techniques, the difficulties of the experimental measurements, the potential for systematic errors, and the number of studies
10 conducted and their agreement or lack thereof. Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurement, i.e. the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 90% confidence limits, of $\pm 10\%$ or less are frequently reported in the literature. Unfortunately,
15 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 uncertainty which is difficult to detect. This is hardly surprising since, unlike molecular reactions, it is not always possible to study atomic and
20 free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise.

The arbitrary assignment of uncertainties made here is based mainly on our state of knowledge of a particular reaction which is dependent upon factors such as the number of independent investigations carried out and the number of different techniques used.
25 On the whole, our assessment of uncertainty limits tends 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 uncertainty limits of a factor of 2 are appropriate.

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

Acknowledgements. The Chairman and members of the Committee wish to express their appreciation to I.U.P.A.C. for the financial help which facilitated the preparation of this evaluation. We also acknowledge financial support from the following organisations: EU Framework Program 6, ACCENT network of excellence; University of California Agricultural Experiment Station; the UK Natural Environmental Research Council; the Standard Reference Data Program (N.I.S.T); the Fonds National Suisse de la Recherche Scientifique (F.N.S.R.S.) and the Office Fédéral de l'Éducation et de la Science, and the Deutsche Forschungsgemeinschaft (SFB 357).

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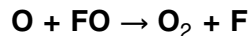
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Appendix 1: FO_x Reactions

III.A1.1



$$\Delta H^\circ = -279 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.7 \pm 0.2) \times 10^{-11}$	298	Bedzhanyan et al., 1993	DL-LMR (a)

Comments

(a) Pseudo-first-order decays of FO radicals in the presence of excess O(³P) atoms were monitored by LMR. O(³P) atom concentrations were determined by EPR.

10 Preferred Values

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

Reliability

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

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Comments on Preferred Values

The preferred value is based on the results of the study of Bedzhanyan et al. (1993), the sole study of this reaction. The temperature dependence of the rate constant is expected to be small for such an atom-radical process, as for the analogous ClO radical reaction.

References

Bedzhanyan, Y. R., Markin, E. M., Politenkova, G. G., and Gershenzon, Y. M.: Kinet. Catal., 33, 797, 1993; original pages 998–1003, 1992.

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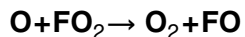
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III.A1.2



$$\Delta H^\circ = -166 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data: no available experimental data.

Preferred Values

$$k = 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

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

Comments on Preferred Values

There are no experimental data for this reaction. The rate constant for such a radical-atom process is expected to approach the gas collision frequency and is not expected to exhibit a strong temperature dependence.

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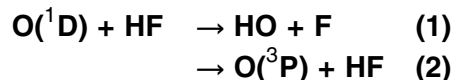
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III.A1.3



$$\Delta H^\circ(1) = -49 \text{ kJ}\cdot\text{mol}^{-1}$$

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

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(5.1 \pm 1.0) \times 10^{-11}$	298	Sorokin et al., 1998, 1999	PLP-LMR (a)
<i>Branching Ratios</i>			
$k_1/k = 0.30 \pm 0.02$	298	Sorokin et al., 1998, 1999	PLP-LMR (a)
$k_2/k = 0.70 \pm 0.02$	298		

Comments

(a) Measured rate coefficient ratio of $k(\text{O}(^1\text{D})+\text{HF})/k(\text{O}(^1\text{D})+\text{NF}_3)$ was placed on an absolute basis by use of the rate coefficient for the reference reaction $k(\text{O}(^1\text{D})+\text{NF}_3)=1.15 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Sorokin et al., 1998, 1999). Pressure in the reactor was ~ 13 mbar.

Preferred Values

$k = 5.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_1/k = 0.30$ at 298 K.

$k_2/k = 0.70$ at 298 K.

5 *Reliability*

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

$\Delta (k_1/k) = \Delta (k_2/k) = \pm 0.1$

Comments on Preferred Values

10 The preferred values of k , k_1/k and k_2/k are based on the results reported by Sorokin et al. (1998, 1999). These results are given in the only published journal articles presenting a systematic study of this system. In a published paper on the reactions of $\text{O}(^1\text{D})$ with HCl and HBr, Wine et al. (1986), because of uncertainties in the HF concentration, report for the reaction $\text{O}(^1\text{D}) + \text{HF}$ only a highly uncertain rate constant in the range $(6\text{--}24) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature.

15 **References**

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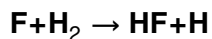
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III.A1.4



$$\Delta H^\circ = -134.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.0 \times 10^{-10} \exp[-(433 \pm 51)/T]$	190–359	Wurzberg and Houston, 1980	PLP-CL
$(2.27 \pm 0.18) \times 10^{-11}$	297		
$(2.55 \pm 0.11) \times 10^{-11}$	298	Clyne and Hodgson, 1985	DF-LIF (a)
$1.2 \times 10^{-10} \exp[-(470 \pm 30)/T]$	221–376	Stevens et al., 1989	DF-RF (b)
$(2.48 \pm 0.09) \times 10^{-11}$	298		

Comments

(a) F atoms were reacted with Br_2 to form BrF which was detected by LIF.

(b) Discharge flow system. F atoms were converted to D atoms by reaction with D_2 downstream of the reaction zone, and the D atoms monitored by resonance fluorescence.

Preferred Values

$k = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.1 \times 10^{-10} \exp(-450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 190–380 K.

Reliability

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

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

Comments on Preferred Values

- 5 This evaluation accepts the recommended values given in the critical review of Persky and Kornweitz (1997) of the literature data for this reaction. The preferred values are based on the results of Wurzburg and Houston (1980), Clyne and Hodgson (1985) and Stevens et al. (1989).

References

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Persky, A. and Kornweitz, H.: Int. J. Chem. Kinet., 29, 67, 1997.
Stevens, P. S., Brune, W. H., and Anderson, J. G.: J. Phys. Chem., 93, 4068, 1989.
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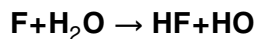
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III.A1.5



$$\Delta H^\circ = -73.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.2 \times 10^{-11} \exp[-(400 \pm 70)/T]$ $(1.1 \pm 0.1) \times 10^{-11}$	243–369 300	Walther and Wagner, 1983	DF-MS
$(1.3 \pm 0.1) \times 10^{-11}$	298 ± 4	Frost et al., 1986	PLP-CL (a)
$1.6 \times 10^{-11} \exp[-(28 \pm 42)/T]$ $(1.42 \pm 0.06) \times 10^{-11}$	240–373 298	Stevens et al., 1989	DF-RF (b)

Comments

- (a) Pulsed laser photolysis of $\text{F}_2\text{-H}_2\text{O-He}$ mixtures at 308 nm, with HF chemiluminescence being monitored.
- (b) Discharge flow system. F atoms were converted to D atoms by reaction with D_2 downstream of the reaction zone. D atoms were monitored by resonance fluorescence.

Preferred Values

$k = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 240–380 K.

Reliability

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

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

Comments on Preferred Values

5 The recommended temperature-independent value is based on the study of Stevens et al. (1989). This value is in good agreement with the room temperature results of Walther and Wagner (1983) and Frost et al. (1986). Walther and Wagner (1983) reported an E/R value of 400 K. Although their data (Walther and Wagner, 1983) have not been used in the derivation of the preferred values, with the exception of the one
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References

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- 15 Stevens, P. S., Brune, W. H., and Anderson, J. G.: *J. Phys. Chem.*, 93, 4068, 1989.
- Walther, C.-D. and Wagner, H. Gg.: *Ber. Bunsenges. Phys. Chem.*, 87, 403, 1983.

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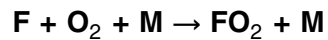
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III.A1.6



$$\Delta H^\circ = -54.0 \text{ kJ}\cdot\text{mol}^{-1}$$

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Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.2 \times 10^{-34} \exp(656/T)$ [He]	272–362	Zetzsch, 1973	DF-MS (a)
4.7×10^{-33} [He]	298		
$(7 \pm 2) \times 10^{-33}$ [He]	293	Arutyunov et al., 1976	DF-EPR
$(1.4 \pm 0.4) \times 10^{-32}$ [N ₂]	293		(b)
$(6 \pm 2) \times 10^{-33}$ [Ar]	293		
$(5.4 \pm 0.6) \times 10^{-33}$ [He]	298	Chen et al., 1977	FP (c)
$(1.5 \pm 0.3) \times 10^{-32}$ [O ₂]	298		
$(5.0 \pm 0.6) \times 10^{-33}$ [F ₂]	298		
$(8.4 \pm 0.9) \times 10^{-33}$ [Ar]	298		
$2.8 \times 10^{-34} \exp(906/T)$ [Ar]	223–293	Shamonima and Kotov, 1979	DF-EPR
$(6.1 \pm 1.8) \times 10^{-33}$ [Ar]	293		(d)
$(1.0 \pm 0.3) \times 10^{-32}$ [O ₂]	298	Chebotarev, 1979	PLP (e)
$(3.2 \pm 2.1) \times 10^{-33}$ [Ar]	298	Smith and Wrigley, 1980	(f)
$(3.7 \pm 2.4) \times 10^{-33}$ [Ar]	298	Smith and Wrigley, 1981	(f)
$(4.3 \pm 0.4) \times 10^{-33} (T/300)^{-1.6}$ [Ar]	295–359	Pagsberg et al., 1987	PR (g)
$(2.8 \pm 0.2) \times 10^{-33}$ [He]	298	Lyman and Holland, 1988	PLP(h)
$(3.1 \pm 0.2) \times 10^{-33}$ [Ar]	298		
1.4×10^{-32} [SF ₆]	295	Ellermann et al., 1994	PR (i)
$5.8 \times 10^{-33} (T/300)^{-1.7}$ [N ₂]	100–373	Campuzano-Jost et al., 1995	PLP (j)

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- (a) Detection of F atoms and FO₂ radicals.
- (b) Detection of F atoms.
- (c) Detection of vibrationally excited HF by IR chemiluminescence.
- 5 (d) Detection of F atoms in the presence of excess O₂ and Ar. Experimental conditions were varied over only limited ranges; for example, [O₂] was varied by a factor of 2 and the total pressure was fixed. The third-order rate coefficient reported for Ar as the diluent gas may be somewhat overestimated as the O₂ ranged from ~12% to ~25% of the total pressure. The stoichiometry was assumed to be 2
- 10 (i.e., $-d[F]/dt=2k[F][O_2][M]$) due to secondary removal of atomic fluorine by reaction with the primary product FO₂.
- (e) Photolysis of WF₆-H₂-O₂-He mixtures at ~200 nm, with detection of HF by IR chemiluminescence. The relative efficiencies of M were reported to be O₂:Ar=1.4:1.0.
- 15 (f) Laser photolysis of F₂-HCl-Ar mixtures in the presence of O₂ at pressures of 100–150 mbar. Vibrational chemiluminescence of HF monitored.
- (g) Experiments were carried out in Ar-F₂-O₂ mixtures with detection of FO₂ by absorption at 220 nm. The rate coefficient and the equilibrium constant were determined by varying the O₂ concentration. A value of $\Delta H^\circ(298\text{ K})=-52.8\text{ kJ mol}^{-1}$
- 20 was derived.
- (h) Photolysis of F₂ at 248 nm in the presence of O₂ and bath gases. The reaction mechanism with 6 reactions was followed via the analysis of transient absorption signals at 215 nm. The forward and backward rate coefficients of the reactions $F+O_2+M\rightarrow FO_2+M$ and $F+FO_2+M\rightarrow F_2O_2+M$ were determined. A value of $\Delta H^\circ(298\text{ K})=-(56.4\pm 1.7)\text{ kJ mol}^{-1}$ was derived.
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- (i) Experiments with SF₆-O₂ mixtures at 0.20–1.0 bar total pressure with kinetic UV spectroscopic detection of FO₂ radicals between 215 and 254 nm. Falloff extrapolations were made with $F_c=0.6$.
- 5 (j) FO₂ radicals were detected by UV absorption. Experiments were carried out at total pressures up to 1000 bar of the bath gases He, Ar, and N₂. Measurements of the equilibrium constant lead to $\Delta H^\circ(0\text{ K})=-49.8\text{ kJ mol}^{-1}$. Falloff extrapolations were made with F_c near 0.5.

Preferred Values

10 $k_0 = 5.8 \times 10^{-33} (T/300)^{-1.7} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 100–380 K.

Reliability

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

$\Delta n = \pm 0.5$

Comments on Preferred Values

15 Because of the large data-base from the study of Campuzano-Jost et al. (1995), their rate coefficients values are preferred and are in reasonable agreement with earlier work. Falloff curves were constructed with F_c near 0.5.

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High-pressure rate coefficients

Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
2.0×10^{-12}	295	Ellermann et al., 1994	PR (a)
1.2×10^{-10}	100–373	Campuzano-Jost et al., 1995	PLP (b)

Comments

- 5 (a) See comment (i) for k_0 .
(b) See comment (j) for k_0 .

Preferred Values

$k_{\infty} = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 100–380 K.

10 Reliability

$\Delta \log k_{\infty} = \pm 0.3$ over the temperature range 100–380 K.

Comments on Preferred Values

15 Because of the large pressure range studied by Campuzano-Jost et al. (1995), a reliable falloff extrapolation towards k_{∞} was possible. The data of Campuzano-Jost et al. (1995) are therefore preferred together with values of F_c near 0.5.

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Intermediate Falloff Range

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	P/Torr	M	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>					
2.4×10^{-13}	600 mbar	SF ₆	298	Wallington and Nielsen, 1991	PR (a)
$(2.35 \pm 0.2) \times 10^{-13}$	600 mbar	SF ₆	298	Wallington et al., 1992	PR (b)

Comments

- 5 (a) Experiments were carried out in mixtures of SF₆ and O₂ (6.1–20 mbar). FO₂ radicals were monitored by UV absorption at 220 nm.
- (b) Experiments were carried out in mixtures of SF₆ and O₂ (2.5–15 mbar). FO₂ radicals were monitored by UV absorption at 220 nm. The results were analyzed together with those of Lyman and Holland (1988).

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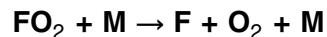
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Interactive Discussion

III.A1.7



$$\Delta H^\circ = 54.0 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
1.8×10^{-17} [Ar]	295	Pagsberg et al., 1987	PR (a)
3.1×10^{-11} [Ar]	312.5		
2.8×10^{-16} [Ar]	359		
$(2.5 \pm 1.0) \times 10^{-18}$ [He]	298	Lyman and Holland, 1988	PLP (b)
$1.0 \times 10^{-5} T^{-1.25} \exp(-5990/T)$ [N ₂]	315–420	Campuzano-Jost et al., 1995	PLP (c)
1.5×10^{-17} [N ₂]	298		

Comments

(a) Experiments were carried out in Ar-F₂-O₂ mixtures with detection of FO₂ by absorption at 220 nm. The rate of approach to equilibrium was monitored and the equilibrium constant measured. A value of $\Delta H^\circ(298 \text{ K})=52.8 \text{ kJ mol}^{-1}$ was derived by a third-law analysis.

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(b) Photolysis of F_2 at 248 nm in the presence of O_2 and bath gases. Transient absorptions at 215 nm were monitored and the approach to equilibrium was analyzed. A value of $\Delta H^\circ(298\text{ K})=56.4\text{ kJ mol}^{-1}$ was derived.

(c) The kinetics were followed by monitoring the FO_2 radical by UV absorption. Experiments were carried out between 100 K and 375 K at total pressures between 1 bar and 1000 bar, and in the bath gases He, Ar, and N_2 . Measurements of the equilibrium constant lead to $\Delta H^\circ(0\text{ K})=49.8\text{ kJ mol}^{-1}$. Falloff extrapolations were carried out with a value of F_c near 0.5. The expression for k_0 was derived from the recombination rate coefficients of the reverse reaction and the equilibrium constants.

Preferred Values

$$k_0 = 1.5 \times 10^{-17} [\text{N}_2] \text{ s}^{-1} \text{ at } 298\text{ K.}$$

$$k_0 = 8.4 \times 10^{-9} (T/300)^{-1.25} \exp(-5990/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 310\text{--}420\text{ K.}$$

Reliability

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

$$\Delta n = \pm 0.5.$$

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

Comments on Preferred Values

The results of Campuzano-Jost et al. (1995) are in reasonable agreement with those of Pagsberg et al. (1987), but differ at 298 K by a factor of 6 with the data from Lyman and Holland (1988). The preferred values are based on the data of Campuzano-Jost et al. (1995).

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High-pressure rate coefficients

Rate coefficient data

k_{∞}/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.3 \times 10^{13} T^{0.45} \exp(-5990/T)$	315–420	Campuzano-Jost et al., 1995	PLP (a)

Comments

- 5 (a) See comment (c) for k_0 .

Preferred Values

$k_{\infty} = 3.1 \times 10^5 \text{ s}^{-1}$ at 298 K.

$k_{\infty} = 1.7 \times 10^{14} (T/300)^{0.45} \exp(-5990/T) \text{ s}^{-1}$ over the temperature range 310–420 K.

Reliability

- 10 $\Delta \log k_{\infty} = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.5$ K.

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

Comments on Preferred Values

- 15 Because of the large pressure range studied by Campuzano-Jost et al. (1995), a reliable falloff extrapolation towards k_{∞} was possible. The data of Campuzano-Jost et al. (1995) are therefore preferred, together with F_c values near 0.5.

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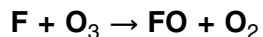
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III.A1.8



$$\Delta H^\circ = -113 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.8 \times 10^{-11} \exp[-(226 \pm 200)/T]$	253–365	Wagner et al., 1972	DF-MS (a)
1.3×10^{-11}	298		
$(6.2 \pm 0.3) \times 10^{-12}$	298	Bedzhanyan et al., 1993	DF-LMR (b)

Comments

(a) MS detection of O_3 decay in the presence of an excess of F atoms. The temporal profiles of F, FO and O_3 were monitored by MS.

(b) Discharge flow system with excess of O_3 over F atoms. Rate of formation of FO radicals was monitored by LMR.

Preferred Values

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

$k = 2.2 \times 10^{-11} \exp(-230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–370 K.

Reliability

$\Delta \log k = \pm 0.25$ at 298 K.

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

Comments on Preferred Values

- 5 The preferred room temperature value is the average of the 298 K values from the two studies of Wagner et al. (1972) and Bedzhanyan et al. (1993). The temperature dependence is taken from Wagner et al. (1972) and the *A*-factor is fitted to the preferred 298 K value. The preferred value at room temperature is supported by values of *k* derived indirectly in studies of the reactions of CF₃O and CF₃O₂ radicals with O₃ by
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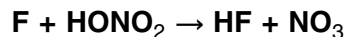
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III.A1.9



$$\Delta H^\circ = -143.9 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

5

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.7 \pm 0.5) \times 10^{-11}$	298	Mellouki et al., 1987	DF-EPR
$(2.1 \pm 1.0) \times 10^{-11}$	298	Rahman et al., 1988	DF-MS
$6.0 \times 10^{-12} \exp[(400 \pm 120)/T]$	260–320	Wine et al., 1988	PLP-A (a)
$(2.3 \pm 0.3) \times 10^{-11}$	298		
$(2.2 \pm 0.2) \times 10^{-11}$	298	Becker et al., 1991	DF-MS
$(2.3 \pm 0.2) \times 10^{-11}$	298	Becker et al., 1991	DF-EPR

Comments

(a) Pulsed laser photolysis of F_2 - HONO_2 -He mixtures at 351 nm, with detection of NO_3 radicals by long-path laser absorption at 662 nm. At higher temperatures (335–373 K) the rate coefficient was observed to be independent of temperature with a value of $(2.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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Preferred Values

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

$k = 6.0 \times 10^{-12} \exp(400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–320 K.

Reliability

5 $\Delta \log k = \pm 0.1$ at 298 K.

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

Comments on Preferred Values

The recommendation is based on the results of the temperature-dependent study of Wine et al. (1988) and the room temperature results of Mellouki et al. (1987), Rahman et al. (1988) and Becker et al. (1991). The values at room temperature are in good agreement. The study of Wine et al. (1988) was over the temperature range 260–373 K; below 320 K the authors fitted their data with the Arrhenius expression recommended here, whereas at higher temperatures a temperature-independent value was found, suggesting the occurrence of different mechanisms in the two temperature regimes.

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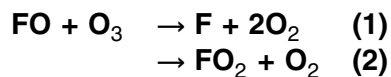
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III.A1.10



$$\Delta H^\circ(1) = -172 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -226 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$< 1.2 \times 10^{-12}$	298	Sehested et al., 1994	PR-UVA (a)
$< 1 \times 10^{-14}$	298	Li et al., 1995	DF-MS (b)

Comments

(a) Pulse radiolysis-UV absorption spectroscopy technique at 18 bar total pressure. FO_2 radicals and O_3 were monitored in absorption at 220 nm and 288 nm, respectively.

(b) Discharge flow-mass spectrometric technique at 1 mbar total pressure. FO radicals were produced in the reaction of F atoms with excess O_3 . No appreciable decay of FO radicals was observed, only a small increase in FO_2 radical concentrations was detected, and the concentration of O_3 was unchanged, allowing the upper limit to k tabulated above to be derived.

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Preferred Values

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

Comments on Preferred Values

The recommended upper limit to the rate coefficient is based on the results of Li et al. (1995). A much higher upper limit was reported by Sehested et al. (1994). A much lower upper limit was derived by Colussi and Grela (1994) from a re-analysis of data that had been reported by Staricco et al. (1962) for ozone destruction quantum yields in the F₂-photosensitized decomposition of ozone. Results of the more direct study of Li et al. (1995) are preferred over the much earlier results reported by Staricco et al. (1962).

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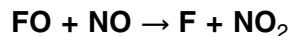
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III.A1.11



$$\Delta H^\circ = -87 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.6 \pm 0.5) \times 10^{-11}$	298	Ray and Watson, 1981	DF-MS
$1.86 \times 10^{-11} (T/300)^{-(0.66 \pm 0.13)}$	300–845	Bedzhanyan et al., 1993	DF-LMR
$(1.9 \pm 0.4) \times 10^{-11}$	300		

Preferred Values

$$k = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 8.2 \times 10^{-12} \exp(300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 290\text{--}850 \text{ K.}$$

Reliability

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

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

Comments on Preferred Values

The preferred room temperature value is the average of the room temperature values from the only two studies of Ray and Watson (1981) and Bedzhanyan et al. (1993).

The temperature dependence is derived from a fit to the data of Bedzhanyan et

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al. (1993) and the *A*-factor is fitted to the preferred 298 K value. The temperature dependence is similar to those for the analogous ClO and BrO radical reactions.

References

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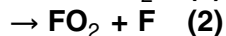
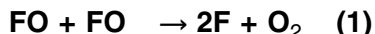
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III.A1.12



$$\Delta H^\circ(1) = -59 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -113 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(3) = -218 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.5 \pm 2.8) \times 10^{-12}$	298	Clyne and Watson, 1974	DF-MS
$1.0 \times 10^{-11} (T/300)^{(0.85 \pm 0.5)}$	300–435	Bedzhanyan et al., 1993	DF-LMR

Preferred Values

10 $k = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 290–440 K.

Reliability

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

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

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Comments on Preferred Values

The recommended value is based on the results of Clyne and Watson (1974) and Bedzhanyan et al. (1993). In a less direct study, Wagner et al. (1972) reported a factor of 3 higher value. Although Bedzhanyan et al. (1993) reported a weak temperature dependence, a temperature-independent rate coefficient fits their data equally well and is recommended in this evaluation. The study of Bedzhanyan et al. (1993) showed that the predominant reaction channel is that to produce $2F+O_2$.

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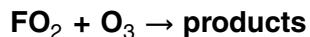
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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$< 3.4 \times 10^{-16}$	298	Sehested et al., 1994	PR-UVA (a)
$< 3 \times 10^{-15}$	298	Li et al., 1995	DF-MS (b)

5 Comments

- (a) Pulse radiolysis of $\text{O}_3\text{-O}_2\text{-SF}_6$ mixtures in a high pressure cell at 18 bar of SF_6 . The decay of FO_2 radicals was monitored in absorption at 220 nm.
- (b) First-order decay rate of FO_2 in presence of excess O_3 at 1.3 mbar (1 Torr) total pressure was monitored by mass spectrometry.

10 Preferred Values

$k < 4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

The preferred room temperature upper limit to the rate coefficient is based on results of the pulse radiolysis-UV absorption study of Sehested et al. (1994). A higher upper
 15 limit was reported by Li et al. (1995).

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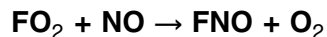
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III.A1.14



$$\Delta H^\circ = -182 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.5 \pm 0.5) \times 10^{-12}$	298	Sehested et al., 1994	PR-UVA (a)
$7.5 \times 10^{-12} \exp[-(688 \pm 377)/T]$	190–298	Li et al., 1995	DF-MS (b)
$(8.5 \pm 1.3) \times 10^{-13}$	298		

Comments

(a) Pulse radiolysis of NO-O₂-SF₆ mixtures at 1 bar SF₆. The formation of FNO was monitored in absorption at 310.5 nm. The yield of FNO was determined to be 100±14%.

(b) First-order decay rates of FO₂ in the presence of excess NO were monitored by mass spectrometry at a total pressure of 1.3 mbar He. The yield of FNO was found to be nearly 100%.

Preferred Values

$k = 7.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 7.5 \times 10^{-12} \exp(-690/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 190–300 K.

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Reliability

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

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

Comments on Preferred Values

5 The preferred values are based on results of the temperature-dependent study of Li et al. (1995). The higher room temperature rate coefficient of Sehested et al. (1994) is encompassed within the assigned uncertainty limits. The low barrier to form FNO may indicate that the reaction proceeds via formation of a short lived FOONO complex (Dibble and Francisco, 1997).

10 References

Dibble, T. S. and Francisco, J. S.: J. Am Chem. Soc., 119, 2894, 1997.

Li, Z., Friedl, R. R., and Sander, S. P.: J. Phys. Chem., 99, 13445, 1995.

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FO₂ + NO₂ → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.05 \pm 0.15) \times 10^{-13}$	298	Sehested et al., 1994	PR-UVA (a)
$3.8 \times 10^{-11} \exp[-(2042 \pm 456)/T]$	260–315	Li et al., 1995	DF-MS (b)
$(4.2 \pm 0.8) \times 10^{-14}$	298		

Comments

- (a) Pulse radiolysis of NO₂-O₂-SF₆ mixtures. The decay of NO₂ was monitored in absorption at 400 nm, and that of FO₂ radicals at 220 nm. The rate coefficient showed no dependence on pressure over the pressure range 1–18 bar of SF₆.
- (b) First-order decay rate of FO₂ radicals in the presence of excess NO₂ was monitored by mass spectrometry at a total pressure of 1.3 mbar He.

Preferred Values

$k = 4.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.8 \times 10^{-11} \exp(-2040/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–320 K.

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Reliability

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

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

Comments on Preferred Values

- 5 The preferred values are based on results of the temperature-dependent study of Li et al. (1995). The higher room temperature result of Sehested et al. (1994) might be attributable to a small NO impurity in the NO₂ sample used. The observed positive temperature dependence suggests that reaction occurs primarily by a simple bimolecular mechanism yielding FNO₂+O₂.

10 References

Li, Z., Friedl, R. R., and Sander, S. P.: J. Phys. Chem., 99, 13445, 1995.

Sehested, J., Sehested, K., Nielsen, O. J., and Wallington, T. J.: J. Phys. Chem., 98, 6731, 1994.

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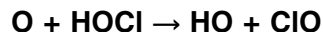
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Appendix 2: ClO_x Reactions

III.A2.16



$$\Delta H^\circ = -32 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.3 \pm 0.2) \times 10^{-13}$	298	Vogt and Schindler, 1992	DF-MS
$(1.7 \pm 0.3) \times 10^{-13}$	213–298	Schindler et al., 1996	DF-MS

Preferred Values

$k = 1.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, independent of temperature over the range 210–300 K.

10 Reliability

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

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

Comments on Preferred Values

15 The preferred values are based on the results of the study of Schindler et al. (1996) in which k was found to be independent of temperature over the range 213–298 K. These results are preferred over those of the previous study of Vogt and Schindler

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(1992) from the same laboratory, which was only at room temperature. In the most recent study (Schindler et al., 1996), product analysis using ^{18}O atoms and ab-initio model calculations indicate that Cl atom abstraction is the predominant primary reaction channel.

5 References

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Vogt, R. and Schindler, R. N.: Geophys. Res. Lett., 19, 1935, 1992.

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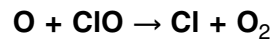
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III.A2.17



$$\Delta H^\circ = -229.5 \text{ kJ}\cdot\text{mol}^{-1}$$

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.3 \pm 0.8) \times 10^{-11}$	298	Bemand et al., 1973	DF-RF
$(5.7 \pm 2.3) \times 10^{-11}$	298	Bemand et al., 1973	DF-MS
$1.07 \times 10^{-10} \exp[-(224 \pm 76)/T]$	220–426	Clyne and Nip, 1976	DF-RF
$(5.2 \pm 1.6) \times 10^{-11}$	298		
$5.2 \times 10^{-11} \exp[-(96 \pm 20)/T]$	236–422	Leu, 1984	DF-RF
$(3.6 \pm 0.7) \times 10^{-11}$	296		
$(4.2 \pm 0.8) \times 10^{-11}$	241–298	Margitan, 1984	PLP-RF
$(3.5 \pm 0.5) \times 10^{-11}$	252–347	Schwab et al., 1984	DF-RF/RA/LMR (a)
$1.55 \times 10^{-11} \exp[(263 \pm 60)/T]$	231–367	Nicovich et al., 1988	PLP-RF (b)
$(3.8 \pm 0.6) \times 10^{-11}$	298		
$3.0 \times 10^{-11} \exp[(75 \pm 40)/T]$	227–362	Goldfarb et al., 2001	PLP-RF (e)
$(3.9 \pm 0.6) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$4.3 \times 10^{-11} \exp[-(4 \pm 30)/T]$	218–295	Zahniser and Kaufman, 1977	RR (c)
$(4.3 \pm 0.7) \times 10^{-11}$	295		
$2.6 \times 10^{-11} \exp[(97 \pm 64)/T]$	220–387	Ongstad and Birks, 1986	RR (d)
$(3.8 \pm 0.6) \times 10^{-11}$	298		

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Comments

(a) Discharge flow system with LMR detection of ClO radicals and resonance fluorescence detection of O(³P) and Cl atoms. Pseudo-first order decay of O(³P) atoms in the presence of excess ClO and decay of ClO in the presence of excess O(³P) gave good agreement for the rate coefficient *k*. There was no discernable temperature dependence over the range studied. The total pressure was in the range 1.1–2.7 mbar.

(b) Dual pulsed laser photolysis system with resonance fluorescence detection in slow flow reactor. ClO radicals were produced by reaction of excess Cl, produced by 351 nm excimer laser photolysis of Cl₂, with known concentrations of O₃. O(³P) atoms were produced by 266 nm laser photolysis of ClO after appropriate delay time, and were monitored by resonance fluorescence. The measured O(³P) atom decay rate was corrected for losses due to reaction with Cl₂ and other routes. The total pressure was in the range 33 mbar to 667 mbar, and no effect of pressure on the rate coefficient *k* was observed.

(c) The rate coefficient *k* was measured relative to *k*(Cl+O₃) using the discharge flow technique in conjunction with resonance fluorescence monitoring of Cl atom concentrations and resonance absorption monitoring of O(³P) atom concentrations in a system where O(³P), Cl, ClO and O₃ had reached a steady-state condition. The tabulated Arrhenius expression was obtained by combining the experimentally determined ratio of $k(\text{O}+\text{ClO})/k(\text{Cl}+\text{O}_3)=1.55 \exp[(246\pm 30)/T]$ with the rate coefficient of $k(\text{Cl}+\text{O}_3)=2.8\times 10^{-11} \exp(-250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).

(d) Discharge flow system with detection of O(³P) atoms by O+NO+M chemiluminescence in the presence of excess ClO. The ClO radical concentrations were determined indirectly by in situ conversion to NO₂ by addition of NO and *k* measured relative to $k(\text{O}+\text{NO}_2\rightarrow\text{NO}+\text{O}_2)=6.58\times 10^{-12} \exp[(-$

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$142 \pm 23/T]$ cm³ molecule⁻¹ s⁻¹, determined concurrently in the same system. The total pressure was 3.1 mbar. No effect of O₂ was observed at 230 K.

(e) Discharge flow tube coupled to a pulsed laser photolysis-resonance fluorescence apparatus. O atoms were produced by PLP of ClO at 308 nm, and their pseudo-first-order decay in excess ClO was monitored by RF. ClO radicals were produced by reaction of excess Cl atoms with O₃ or Cl₂O. Cl atoms were produced in the microwave discharge of a Cl₂-He mixture. The total pressure was in the range 7–29 mbar. In this paper the authors, on the basis of a careful analysis of their data and the existing literature data on this reaction (see Comments on Preferred Values), proposed a temperature-dependent expression to be used for atmospheric calculations.

Preferred Values

$k = 3.7 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

$k = 2.5 \times 10^{-11} \exp(110/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 220–390 K.

Reliability

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

$\Delta (E/R) = \pm 50$ K.

Comments on Preferred Values

The preferred value accepts the recommendation of Goldfarb et al. (2001) based on a careful analysis of their data and data published in previous studies. The data used in the analysis were those published in Zahniser and Kaufman (1977), Margitan (1984), Schwab et al. (1984), Ongstad and Birks (1986), Nicovich et al. (1988) and Goldfarb et al. (2001). On the basis of newer information, the rate coefficients reported

by Zahniser and Kaufman (1977), Margitan (1984) and Ongstad and Birks (1986) were adjusted (Goldfarb et al., 2001). Leu and Yung (1987) have shown that the yields of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ in the reaction are $<2 \times 10^{-2}$ and $(4.4 \pm 1.1) \times 10^{-4}$, respectively.

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- 5 Bemand, P. P., Clyne, M. A. A., and Watson, R. T.: J. Chem. Soc. Faraday Trans., 1, 69, 1356, 1973.
Clyne, M. A. A. and Nip, W. S.: J. Chem. Soc. Faraday Trans., 1, 72, 2211, 1976.
Goldfarb, L., Burkholder, J. B., and Ravishankara, A. R.: J. Phys. Chem. A, 105, 5402, 2001.
- 10 IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>, 2005.
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- 15 Ongstad, A. P. and Birks, J. W.: J. Chem. Phys., 85, 3359, 1986.
Schwab, J. J., Toohey, D. W., Brune, W. H., and Anderson, J. G.: J. Geophys. Res., 89, 9581, 1984.
Zahniser, M. S. and Kaufman, F.: J. Chem. Phys., 66, 3673, 1977.

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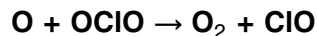
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III.A2.18



$$\Delta H^\circ = -242.2 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5 \pm 2) \times 10^{-13}$	298	Bemand et al., 1973	DF-RF/MS (a)
$(1.6 \pm 0.4) \times 10^{-13}$	298	Colussi, 1990	PLP-RF (b)
See Comment	248–312	Colussi et al., 1992	PLP-RF (c)
$2.4 \times 10^{-12} \exp[-(960 \pm 120)/T]$	243–400	Gleason et al., 1994	DF-RF (d)
$(1.0 \pm 0.3) \times 10^{-13}$	298		

Comments

(a) Discharge flow system. Two independent methods were used: $\text{O}(^3\text{P})$ atom decay in excess OCIO monitored by resonance fluorescence, and OCIO decay in excess $\text{O}(^3\text{P})$ determined by MS. There was only fair agreement between the two methods.

(b) Pulsed laser photolysis of OCIO at 308 nm, with the $\text{O}(^3\text{P})$ atom decay being determined by resonance fluorescence. The results were extrapolated to zero laser pulse intensity. Measurements were made over the pressure range 13 mbar to 1040 mbar of Ar. The observed rate coefficients were pressure dependent, indicating the presence of a termolecular association reaction. The value reported

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for the bimolecular component was not directly measured but was derived from fitting a falloff curve to the experimental data over the entire pressure range.

(c) Pulsed laser photolysis of OCIO at 308 nm, with the O(³P) atom decay being determined by resonance fluorescence. The observed rate coefficients were pressure dependent, indicating the presence of a termolecular association reaction. A negative temperature dependence was observed for the bimolecular component, with the reported values of k increasing from $1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 312 K to $4.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 248 K. These values for the bimolecular component were not directly measured but were derived quantities which are consistent with falloff curves fitted to the experimental data over the pressure range 26 mbar to 800 mbar of Ar.

(d) Discharge flow system with resonance fluorescence detection of O(³P) atoms. The total pressure was 1 mbar to 7 mbar. Measurements were made over the temperature range 200 K to 400 K. The data for the temperature range 243 K to 400 K were fitted with the Arrhenius expression given in the table. Data at lower temperatures showed a negative temperature dependence.

Preferred Values

$k = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.4 \times 10^{-12} \exp(-960/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–400 K.

Reliability

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

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

The preferred values are based on the results of the discharge flow-resonance fluorescence study of Gleason et al. (1994). Over the temperature range of the recommendation (240 K to 400 K), the data of Gleason et al. (1994) were well fit by the Arrhenius expression given, but at lower temperatures down to 200 K there was an abrupt change to a negative temperature dependence (Gleason et al., 1994). It appears that the experiments of Bemand et al. (1973) were complicated by secondary chemistry. The experiments of Colussi (1990) and Colussi et al. (1992) over an extended pressure range demonstrate the importance of the termolecular reaction (see separate data sheet on O+OCIO+M). However, the extrapolated low pressure rate coefficients of Colussi (1990) and Colussi et al. (1992) show a negative temperature dependence over the range 248 K to 312 K, in contrast to the data of Gleason et al. (1994). Mauldin et al. (1997) have studied the mechanism and products of this system at 260 K and a total pressure of 430 mbar of N₂. Under these conditions the value of the rate coefficient for the reaction O+OCIO → products was reported to be $1.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Mauldin et al., 1997). Combining this overall rate coefficient with the observation that the yield of ClO radicals under these conditions is <5% (Mauldin et al., 1997), leads to an upper limit of $k(\text{O}+\text{OCIO} \rightarrow \text{O}_2+\text{ClO}) < 1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 260 K. This upper limit to the rate coefficient is consistent with the value of Gleason et al. (1994), but not with the extrapolated values of Colussi et al. (1992).

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$$\Delta H^\circ = -126.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.4 \pm 0.3) \times 10^{-31} [\text{Ar}]$	298	Colussi, 1990	PLP-RF (a)
$1.9 \times 10^{-31} (T/298)^{-1.1} [\text{Ar}]$	248–312	Colussi et al., 1992	PLP-RF (b)

Comments

(a) Pulsed laser photolysis of OCIO at pressures of Ar between 10 and 1000 mbar. The oxygen atoms produced were detected by resonance fluorescence. Fit of the falloff curve used $F_c=0.6$.

(b) See comment (a). The falloff curves were fitted with $F_c=0.5$ at 248 K, 0.48 at 273 K, and 0.45 at 312 K.

Preferred Values

$k_0 = 1.8 \times 10^{-31} (T/298)^{-1} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–320 K.

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Reliability

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

$\Delta n = \pm 0.5$

Comments on Preferred Values

- 5 The preferred values are based on the data of Colussi et al. (1992) using falloff extrapolations with a fitted value of $F_c=0.5$ at 298 K. Low pressure experiments by Gleason et al. (1994) (1.3–7 mbar) indicate the presence of the reaction $O+OCIO \rightarrow ClO+O_2$.

High-pressure rate coefficients

10 Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.1 \pm 0.8) \times 10^{-11}$	298	Colussi, 1990	PLP-RF (a)
2.8×10^{-11}	248–312	Colussi et al., 1992	PLP-RF (b)

Comments

(a) See comment (a) for k_0 .

(b) See comment (b) for k_0 .

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Preferred Values

$k_{\infty} = 2.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 240–320 K.

Reliability

- 5 $\Delta \log k_{\infty} = \pm 0.3$ at 298 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

See comments on k_0 . The rate coefficients of Colussi et al. (1992) were confirmed by measurements carried out by Mauldin et al. (1997) at 260 K and 430 mbar of N_2 .
10 Under these conditions (260 K and 430 mbar of N_2), Mauldin et al. (1997) observed that the reaction led to the formation of ClO radicals with a yield of <5%. Mauldin et al. (1997) concluded that the combination reaction may involve the intermediate formation of a species such as OOCIO which is different from ClO_3 and which does not rearrange to give $\text{O}_2 + \text{ClO}$.

15 Theoretical modelling of the reaction by Zhu and Lin (2002) led to values of k_{∞} which were a factor of 5–7 higher than obtained from the measurements. As the measurements of Colussi et al. (1992) look well-behaved, they are preferred to the modelling. There is also still some dispute about the heat of reaction, see the calculations by Sicre and Cobos (2003).

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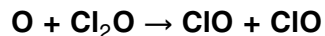
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III.A2.20



$$\Delta H^\circ = -123 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

5

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.7 \times 10^{-11} \exp[-(560 \pm 80)/T]$ $(4.1 \pm 0.5) \times 10^{-12}$	236–295 295	Miziolek and Molina, 1978	DF-CL
$3.3 \times 10^{-11} \exp[-(700 \pm 150)/T]$ $(3.1 \pm 0.5) \times 10^{-12}$	237–297 297	Wecker et al., 1982	DF-EPR
$2.7 \times 10^{-11} \exp[-(510 \pm 30)/T]$ $(4.7 \pm 0.2) \times 10^{-12}$	230–380 298	Stevens and Anderson, 1992	DF-RF

Preferred Values

$k = 4.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.7 \times 10^{-11} \exp(-530/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–380 K.

10

Reliability

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

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

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Comments on Preferred Values

The preferred value at 298 K is based on the results of Stevens and Anderson (1992) and Miziolek and Molina (1978), which are in good agreement. The significantly lower values of Wecker et al. (1982) are not included, nor are earlier, higher results of Freeman and Phillips (1968) and Basco and Dogra (1971) due to data analysis difficulties in both studies (Freeman and Phillips, 1968; Basco and Dogra, 1971).

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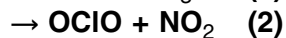
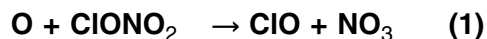
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III.A2.21



$$\Delta H^\circ(1) = -96.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -144.3 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(3) = -216 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.0 \pm 0.2) \times 10^{-13}$	245	Ravishankara et al., 1977	FP-RF
$3.4 \times 10^{-12} \exp[-(840 \pm 60)/T]$	213–295	Molina et al., 1977	DF-CL
$(2.0 \pm 0.4) \times 10^{-13}$	295		
$1.9 \times 10^{-12} \exp[-(692 \pm 167)/T]$	225–273	Kurylo, 1977	FP-RF
1.8×10^{-13}	298*		
$(2.3 \pm 0.6) \times 10^{-13}$	298	Adler-Golden and Wiesenfeld, 1981	FP-RA
$(2.4 \pm 0.4) \times 10^{-13}$	298	Tyndall et al., 1997	PLP-RF
$4.5 \times 10^{-12} \exp[-(900 \pm 80)/T]$	202–325	Goldfarb et al., 1998	PLP-RF/A
$(2.2 \pm 0.2) \times 10^{-13}$	298		(a)

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(a) k was measured by two independent techniques: (1) pulsed laser photolysis with time-resolved resonance fluorescence detection of O-atom decay, and (2) pulsed laser photolysis with time-resolved long-path absorption at 662 nm by the product NO_3 radical. The yield of NO_3 radicals produced in the reaction was also measured in the long-path absorption apparatus.

Preferred Values

$k = 2.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 4.5 \times 10^{-12} \exp(-900/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–330 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are based on the results of the study of Goldfarb et al. (1998). This study encompassed the broadest range of experimental conditions and used two completely different techniques. Results obtained by these two techniques were in complete agreement. Results of the earlier temperature dependent studies of Molina et al. (1977) and Kurylo (1977) and the room temperature studies of Adler-Golden and Wiesenfeld (1981) and Tyndall et al. (1997) are in good agreement with the preferred values.

Using the long-path absorption apparatus to monitor NO_3 radicals, Goldfarb et al. (1998) measured the yield of the NO_3 radical produced in this reaction to be ap-

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proximately unity. Allowing for uncertainties in the measurements Goldfarb et al. (1998) concluded that NO_3 and ClO radicals are the primary products of this reaction and account for at least 70% of the reaction over the temperature range studied (248 K to 298 K).

5 References

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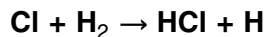
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$$\Delta H^\circ = 4.4 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

5

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.0 \times 10^{-11} \exp[-(2164 \pm 101)/T]$	251–456	Westenberg and de Haas, 1968	DF-EPR
$(1.35 \pm 0.07) \times 10^{-14}$	297		
$(1.26 \pm 0.10) \times 10^{-14}$	298	Davis et al., 1970	FP-RF (a)
$5.5 \times 10^{-11} \exp[-(2391 \pm 50)/T]$	213–350	Watson et al., 1975	FP-RF
$(1.80 \pm 0.2) \times 10^{-14}$	298		
$2.66 \times 10^{-11} \exp[-(2230 \pm 60)/T]$	200–500	Lee et al., 1977	FP-RF
$(1.77 \pm 0.13) \times 10^{-14}$	302		
$3.65 \times 10^{-11} \exp[-(2310 \pm 20)/T]$	199–499	Miller and Gordon, 1981	FP-RF
$(1.49 \pm 0.07) \times 10^{-14}$	298.1±0.5		
$6.00 \times 10^{-11} \exp[-(2470 \pm 100)/T]$	297–425	Kita and Stedman, 1982	DF-RF
$(1.46 \pm 0.22) \times 10^{-14}$	297		
$4.4 \times 10^{-11} \exp(-2568/T)$	291–1283	Adusei and Fontijn, 1994,	FP/PLP-RF
8.1×10^{-15}	291		
$(1.68 \pm 0.22) \times 10^{-14}$	296	Kumaran et al., 1994	PLP-RA (b)

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Comments

(a) Rate coefficient has been decreased by 10%, as recommended by the NASA evaluation panel (NASA, 1997).

(b) Rate coefficients also measured over the temperature range 699–2939 K, and a combination of the 296 K and 699–2939 K rate coefficients resulted in $k = 4.78 \times 10^{-16} T^{1.58} \exp(-1610/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

$k = 1.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.9 \times 10^{-11} \exp(-2310/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–310 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are derived from a least-squares fit to the rate coefficients measured at $\leq 302 \text{ K}$ by Watson et al. (1975), Lee et al. (1977), Miller and Gordon (1981), Kita and Stedman (1982) and Kumaran et al. (1994). The results of these studies are in excellent agreement below $\sim 300 \text{ K}$; at higher temperatures the data are in poorer agreement. The two studies of Miller and Gordon (1981) and Kita and Stedman (1982) have measured both the forward and reverse rates and have shown that the rate

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coefficient ratio agrees with equilibrium constant data. The room temperature rate coefficients of Adusei and Fontijn (1994) are in reasonable agreement with the preferred values.

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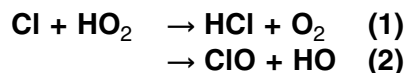
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III.A2.23



$$\Delta H^\circ(1) = -228.2 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = 2.9 \text{ kJ}\cdot\text{mol}^{-1}$$

5

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.23 \pm 0.07) \times 10^{-11}$	250–414	Lee and Howard, 1982	DF-LMR (a)
$k_1 = (4.4 \pm 1.5) \times 10^{-11}$	308	Cattell and Cox, 1986	MM(b)
$k_2 = (9.4 \pm 1.9) \times 10^{-12}$	308		
$3.8 \times 10^{-11} \exp[(40 \pm 90)/T]$	230–360	Riffault et al., 2001	DF-MS (c)
$(4.4 \pm 0.5) \times 10^{-11}$	300		
$k_2 = 8.6 \times 10^{-11} \exp[-(660 \pm 100)/T]$	230–360		
$k_2 = (9.9 \pm 2.8) \times 10^{-12}$	295		
<i>Branching Ratio</i>			
$k_2/k = 1.09 \exp(-478/T)$	250–414	Lee and Howard, 1982	DF-LMR (a)

Comments

(a) On the basis of the temperature independent overall rate coefficient and the temperature dependent branching ratio, the authors derived the rate

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coefficient expressions $k_1 = 1.8 \times 10^{-11} \exp[(170 \pm 80)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_2 = 4.1 \times 10^{-11} \exp[-(450 \pm 60)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

(b) Rate coefficients were derived from the observed time-concentration behavior of HO₂ and ClO radicals using computer simulations and a 25-step reaction mechanism. Because of uncertainties in the Cl atom concentrations, the rate coefficients k_1 and k_2 cited above (for 1 bar total pressure) may be low by a factor of 2 and high by a factor of 2, respectively (Cattell and Cox, 1986). The reaction was also studied over the pressure range 67 mbar to 1013 mbar, and no pressure dependence of either k_1 or k_2 over this range was evident.

(c) k was determined under pseudo-first order conditions with either HO₂ or Cl in excess. Because the reported weak temperature dependence is not significantly different from zero, a temperature independent rate coefficient $k = (4.4 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, was also reported for the temperature range 230–360 K. k_2 was determined from the formation kinetics of both OH and ClO.

Preferred Values

$k_1 = 3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2 = 9.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 4.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, over the temperature range 230–420 K.

$k_2 = 6.3 \times 10^{-11} \exp(-570/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 230–420 K.

Reliability

$\Delta \log k_1 = \pm 0.2$ at 298 K.

$\Delta \log k_2 = \pm 0.2$ at 298 K.

$$\Delta (E_2/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The preferred values for k_1 and k_2 are based on results of the direct studies of Lee and Howard (1982) and Riffault et al. (2001) which are in very good agreement. The total rate coefficient is temperature independent over the range 230 K to 420 K with a value of $4.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and the room temperature results of Cattell and Cox (1986) are in agreement with this recommendation. Based on the combined results of these studies, neither channel shows any pressure dependence between 1 mbar and 1 bar showing that stabilization of the HOOCI^* intermediate does not occur, the two bimolecular channels making up the entire reaction pathway. The preferred Arrhenius expression for k_2 is based on the mean of the E/R values from the temperature dependence studies of Lee and Howard (1982) and Riffault et al. (2001), combined with a pre-exponential factor adjusted to give the preferred value of k_2 at 298 K. Dobis and Benson (1993) report a total rate coefficient in good agreement with this recommendation but a significantly lower value of the branching ratio k_2/k . Results of earlier indirect studies (Leu and DeMore, 1976; Poulet et al., 1978; Burrows et al., 1979; Cox, 1980) were not used in the evaluation of the preferred values.

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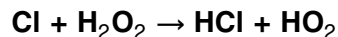
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III.A2.24



$$\Delta H^\circ = -62.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.8_{-2.9}^{+5.8}) \times 10^{-13}$	298	Watson et al., 1976	FP-RF (a)
$(6.2 \pm 1.5) \times 10^{-13}$	295	Leu and DeMore, 1976	DF-MS
$1.24 \times 10^{-12} \exp[-(384 \pm 168)/T]$	265–400	Michael et al., 1977	FP-RF (b)
$(3.64 \pm 0.52) \times 10^{-13}$	299		
$(4.0 \pm 0.4) \times 10^{-13}$	298	Poulet et al., 1978	DF-MS
$1.05 \times 10^{-11} \exp[-(982 \pm 102)/T]$	298–424	Keyser, 1980	DF-RF
$(4.1 \pm 0.2) \times 10^{-13}$	298		

Comments

- (a) A recalculated rate coefficient of $(5.2_{-2.9}^{+5.8}) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is cited in Michael et al. (1977).
- (b) Obtained using H_2O_2 concentrations measured after the reaction cell. Using an average of the H_2O_2 concentrations measured in the reactant flow prior to and after the reaction cell, a rate coefficient of $k = (3.14 \pm 0.56) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 265–400 K, was obtained.

Preferred Values

$k = 4.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.1 \times 10^{-11} \exp(-980/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–430 K.

5 Reliability

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

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

Comments on Preferred Values

10 The room temperature rate coefficients measured by Watson et al. (1976), Leu and DeMore (1976), Michael et al. (1977), Poulet et al. (1978) and Keyser (1980) cover the range $(3.6\text{--}6.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The studies of Michael et al. (1977), Poulet et al. (1978) and Keyser (1980) are considered to be the most reliable. The recommended Arrhenius expression is that reported by Keyser (1980). The rate coefficient measured by Michael et al. (1977) at 265 K is in good agreement with the recommendation; however, the *A*-factor reported is considerably lower than that expected
15 from theoretical considerations and may be attributed to decomposition of H₂O₂ above 300 K (which was indeed observed, especially at 400 K). More data are required before the Arrhenius parameters can be considered to be well established. Heneghan and Benson (1983), using mass spectrometry, confirmed that this reaction proceeds
20 only by the H-atom abstraction mechanism.

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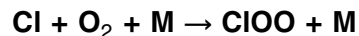
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III.A2.25



$$\Delta H^\circ = -23.8 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.6 \times 10^{-34} [\text{Ar}]$	200–300	Clyne and Coxon, 1968	DF (a)
$1.7 \times 10^{-33} [\text{N}_2 + \text{O}_2]$	300	Nicholas and Norrish, 1968	FP-UVA (b)
$(8.9 \pm 2.9) \times 10^{-33} [\text{O}_2]$	186.5	Nicovich et al., 1991	PLP-RF (c)
$1.6 \times 10^{-33} (T/300)^{-2.9} [\text{O}_2]$	160–260	Baer et al., 1991	PLP-UVA
$(6.3 \pm 1.2) \times 10^{-33} [\text{O}_2]$	186.5		(d)
$1.4 \times 10^{-33} (T/300)^{-3.9} [\text{N}_2]$	160–260	Baer et al., 1991	PLP-UVA (d)

Comments

- (a) Measurements attributed to D. H. Stedman. Cl atoms were monitored by chlorine afterglow emission.
- 10 (b) Rate coefficients were determined by a complex analysis of the time-resolved production of ClO radicals in the photolysis of Cl₂-O₂ mixtures. ClO radicals were measured by photographic recording of their absorption.

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(c) Photolysis of $\text{Cl}_2\text{-O}_2$ mixtures at 181–200 K and with O_2 pressures of 20–53 mbar. Detection of $\text{Cl}(^2\text{P}_{3/2})$ atoms. An equilibrium constant for the reaction of $K_p=18.9 \text{ bar}^{-1}$ was determined at 185.4 K.

(d) Photolysis of $\text{Cl}_2\text{-O}_2\text{-M}$ mixtures with $\text{M}=\text{He}, \text{Ar}, \text{O}_2$ and N_2 , with detection of ClOO radicals. Redetermination of the ClOO radical absorption cross-sections gave $\sigma(248 \text{ nm})=3.4 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. Measurements over the temperature range 160–260 K and the pressure range 1–1000 bar were in agreement with the data of Mauldin et al. (1992). Negligible deviations from third-order behavior were observed at pressures below 10 bar. At higher pressures, an anomalous transition to a high pressure plateau was observed. This and the anomalously strong temperature dependence suggest that the reaction proceeds on a radical-complex instead of the usual energy transfer mechanism. An equilibrium constant of $K_p=5.3 \times 10^{-6} \exp(23.4 \text{ kJ mol}^{-1}/RT) \text{ bar}^{-1}$ was determined over the temperature range 180 K to 300 K.

Preferred Values

$k_0 = 1.4 \times 10^{-33} (T/300)^{-3.9} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 160–300 K.

$k_0 = 1.6 \times 10^{-33} (T/300)^{-2.9} [\text{O}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 160–300 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 200 K.

$\Delta n = \pm 1$.

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The two recent studies of Nicovich et al. (1991) and Baer et al. (1991) are in good agreement and are also consistent with the older data of Nicholas and Norrish (1968), if one takes into account the strong temperature dependence of k_0 . The most extensive measurements of Baer et al. (1991) are the basis for the preferred values. No falloff expressions are reported here, because deviations from third-order behavior become apparent only at pressures higher than 10 bar and because the falloff formalism does not apply to the radical-complex mechanism which is probably operating in this case.

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- 15 Nicholas, J. E. and Norrish, R. G. W.: Proc. Roy. Soc. London, A, 307, 391, 1968.
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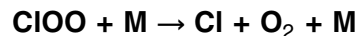
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Interactive Discussion

III.A2.26



$$\Delta H^\circ = 23.8 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.9 \times 10^{-14} [\text{O}_2]$	185.4	Nicovich et al., 1991	PLP-RF (a)
$2.8 \times 10^{-10} \exp(-1820/T) [\text{N}_2]$	160–260	Baer et al., 1991	PLP-UVA
$6.2 \times 10^{-13} [\text{N}_2]$	298*		(a)
$6.3 \times 10^{-10} \exp(-2030/T) [\text{O}_2]$	160–260	Baer et al., 1991	PLP-UVA
$1.1 \times 10^{-14} [\text{O}_2]$	185.4		(a)

Comments

(a) From measurements of the reverse reaction and the equilibrium constant.

Preferred Values

10 $k_0 = 6.2 \times 10^{-13} [\text{N}_2] \text{ s}^{-1}$ at 298 K.

$k_0 = 2.8 \times 10^{-10} \exp(-1820/T) [\text{N}_2] \text{ s}^{-1}$ over the temperature range 160–300 K.

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Reliability

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

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

Comments on Preferred Values

- 5 The preferred values are based on the extensive data of Baer et al. (1991). No deviations from third-order behavior were observed at pressures below 1 bar. The reaction probably does not proceed via an energy-transfer mechanism (see comments on the reverse reaction $\text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{ClOO} + \text{M}$), but rather by a radical-complex mechanism.

References

- 10 Baer, S., Hippler, H., Rahn, R., Siefke, M., Seitzinger, N., and Troe, J.: J. Chem. Phys., 95, 6463, 1991.
Nicovich, J. M., Kreutter, K. D., Shackelford, C. J., and Wine, P. H.: Chem. Phys. Lett., 179, 367, 1991.

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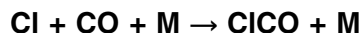
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III.A2.27



$$\Delta H^\circ = 32.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.1 \pm 3.0) \times 10^{-34}$ [Ar]	300	Clark et al., 1966	DF (a)
$1.05 \times 10^{-34} \exp[(810 \pm 70)/T]$ [N ₂]	185–260	Nicovich et al., 1990	PLP-RF (b)
1.6×10^{-33} [N ₂]	298		
<i>Relative Rate Coefficients</i>			
$(1.4 \pm 0.3) \times 10^{-33}$ [N ₂]	298	Hewitt et al., 1996	(c)

Comments

(a) Cl atoms were generated from the photolysis of Cl₂-He mixtures and were measured by titration with nitrosyl chloride using the red chlorine afterglow spectrum. The total pressure was 2.7–5.3 mbar. From additional experiments carried out at 195 K, an activation energy of about -8.4 kJ mol^{-1} was obtained.

(b) Pulsed laser photolysis of Cl₂-CO-M (M=N₂, CO, Ar and CO₂) mixtures at 355 nm. The pressure was 19–267 mbar. By second- and third-law analyses of the temperature dependence of the equilibrium constant, a value of $\Delta H^\circ(298 \text{ K}) = -(32.2 \pm 2.5) \text{ kJ mol}^{-1}$ was derived. The relative collision efficiencies were $\beta_c(\text{CO}_2) : \beta_c(\text{CO/N}_2) : \beta_c(\text{Ar}) = 3.2 : 1.0 : 0.8$.

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(c) Steady state photolysis of Cl₂ in the presence of CO and a reference gas (CH₄ or CHCl₃). Long-path FTIR spectroscopy of CO and CO₂. Measurements of k_0 in 1 bar of air at 298 K relative to $k(\text{Cl}+\text{CH}_4)=1.0\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$.

Preferred Values

5 $k_0 = 1.3 \times 10^{-33} (T/300)^{-3.8} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 180–300 K.

Reliability

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

$\Delta n = \pm 1$.

10 *Comments on Preferred Values*

The recommended rate coefficients are based on the measurements of Nicovich et al. (1990) which agree well with the relative rate measurements from Hewitt et al. (1996). No signs of deviations from third-order behavior were detected.

References

- 15 Clark, T. C., Clyne, M. A. A., and Stedman, D. H.: Trans. Faraday Soc., 62, 3354, 1966.
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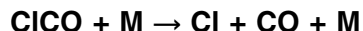
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III.A2.28



$$\Delta H^\circ = 32.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.1 \times 10^{-10} \exp[-(2960 \pm 160)/T] [\text{N}_2]$	185–260	Nicovich et al., 1990	PLP-RF (a)

Comments

(a) Pulsed laser photolysis of $\text{Cl}_2\text{-CO-M}$ ($\text{M}=\text{N}_2$, CO , Ar and CO_2) mixtures at 355 nm. The pressure was 19–267 mbar. By second- and third-law analyses of the temperature dependence of the equilibrium constant, a value of $\Delta H^\circ(298 \text{ K})=(32.2\pm 2.5) \text{ kJ mol}^{-1}$ was derived. The relative collision efficiencies were $\beta_c(\text{CO}_2) : \beta_c(\text{CO}/\text{N}_2) : \beta_c(\text{Ar}) = 3.2 : 1.0 : 0.8$.

Preferred Values

$$k_0 = 2.0 \times 10^{-14} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

15 $k_0 = 4.1 \times 10^{-10} \exp(-2960/T) [\text{N}_2] \text{ s}^{-1}$ over the temperature range 180–300 K.

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Reliability

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

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

Comments on Preferred Values

- 5 The preferred rate coefficients are based on the study of Nicovich et al. (1990).

References

Nicovich, J. M., Kreutter, K. D., and Wine, P. H.: J. Chem. Phys., 92, 3539, 1990.

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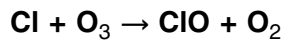
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III.A2.29



$$\Delta H^\circ = -162.4 \text{ kJ}\cdot\text{mol}^{-1}$$

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.08 \times 10^{-11} \exp[-(290 \pm 25)/T]$	220–350	Watson et al., 1976	FP-RF
$(1.20 \pm 0.10) \times 10^{-11}$	298		
$2.17 \times 10^{-11} \exp[-(171 \pm 30)/T]$	205–366	Zahniser et al., 1976	DF-RF (a)
$(1.23 \pm 0.25) \times 10^{-11}$	298		
$2.72 \times 10^{-11} \exp[-(298 \pm 39)/T]$	213–298	Kurylo and Braun, 1976	FP-RF (a)
$(1.02 \pm 0.15) \times 10^{-11}$	298		
$5.18 \times 10^{-11} \exp[-(418 \pm 28)/T]$	221–629	Clyne and Nip, 1976	DF-RF
$(1.33 \pm 0.26) \times 10^{-11}$	298		
$(1.3 \pm 0.3) \times 10^{-11}$	295	Leu and DeMore, 1976	DF-MS (b)
$(1.3 \pm 0.2) \times 10^{-11}$	298	Toohey et al., 1988	DF-RF
$2.49 \times 10^{-11} \exp[-(233 \pm 46)/T]$	269–385	Nicovich et al., 1990	PLP-RF (c)
$1.19 \times 10^{-11} \exp[-(33 \pm 37)/T]$	189–269		
$(1.14 \pm 0.17) \times 10^{-11}$	298		
$1.59 \times 10^{-11} \exp[-(87 \pm 57)/T]$	206–296	Seeley et al., 1996	DF-RF (d)
$(1.21 \pm 0.13) \times 10^{-11}$	295		
$3.1 \times 10^{-11} \exp[-(280 \pm 100)/T]$	184–298	Beach et al., 2002	DF-RF
$(1.41 \pm 0.08) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
1.17×10^{-11}	197	DeMore, 1991	RR (e)
1.24×10^{-11}	217		

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Comments

(a) The A -factors tabulated are $\sim 8\%$ lower than those originally reported due to a revision of the value used for the O_3 absorption cross-sections.

(b) Discharge flow system with MS detection of O_3 .

(c) A change in slope of the Arrhenius plot was observed at ~ 270 K. The data were fitted to two separate Arrhenius expressions over the temperature ranges 189–269 K and 269–385 K.

(d) Turbulent flow conditions were used with total pressures in the range 66 mbar to 330 mbar.

(e) Competitive chlorination of O_3 - CH_4 mixtures. Cl atoms were produced by the photolysis of Cl_2 at 300 nm to 400 nm. The measured rate coefficient ratios $k(Cl+O_3)/k(Cl+CH_4)$ are placed on an absolute basis using a rate coefficient of $k(Cl+CH_4)=6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Vanderzanden and Birks, 1982).

Preferred Values

$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.8 \times 10^{-11} \exp(-250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 180–300 K.

Reliability

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

$\Delta (E/R) = {}_{-150}^{+100} \text{ K}$.

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The majority of the rate coefficients for this reaction have been obtained at temperatures at and below 298 K, and our evaluation is restricted to that temperature regime. The preferred value of k at 298 K is the mean of the absolute room temperature rate coefficients of Watson et al. (1976), Zahniser et al. (1976), Kurylo and Braun (1976), Clyne and Nip (1976), Leu and DeMore (1976), Toohey et al. (1988), Nicovich et al. (1990) and Seeley et al. (1996), all of which are in excellent agreement. In the recent study of Beach et al. (2002) a slightly but significantly higher value was obtained at 298 K, but the Arrhenius expression for k derived by Beach et al. (2002) from the results over the whole temperature range covered gives a value of $k(298\text{ K})$ in excellent agreement with the recommended value. The Arrhenius temperature dependence of k is obtained from a least-squares fit to all of the data at and below 298 K from the studies of Watson et al. (1976), Zahniser et al. (1976), Kurylo and Braun (1976), Clyne and Nip (1976), Leu and DeMore (1976), Toohey et al. (1988) and Beach et al. (2002). This temperature dependence is combined with a pre-exponential factor adjusted to fit the value of k at 298 K.

Nicovich et al. (1990) observed non-Arrhenius behavior in the temperature range studied (189 K to 385 K). The data of Nicovich et al. (1990) are in excellent agreement with the present recommendation above $\sim 250\text{ K}$; at lower temperatures their data are higher than the recommendation although still within the stated uncertainty down to $\sim 220\text{ K}$.

Vanderzanden and Birks (1982) have interpreted their observation of oxygen atoms in this system as evidence for some production (0.1% to 0.5%) of $\text{O}_2(^1\Sigma_g)$ in this reaction. The possible production of singlet molecular oxygen in this reaction has also been discussed by DeMore (1981) in connection with the Cl_2 photosensitized decomposition of ozone. However, Choo and Leu (1985) were unable to detect $\text{O}_2(^1\Sigma)$ or $\text{O}_2(^1\Delta)$ in the $\text{Cl}+\text{O}_3$ system and set upper limits to the branching ratios for their production of 5×10^{-4} and 2.5×10^{-2} , respectively. A crossed molecular beam study

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(Zhang and Lee, 1997) also found no evidence for the production of electronically excited O_2 . Choo and Leu (1985) suggested two possible mechanisms for the observed production of oxygen atoms, involving reactions of vibrationally excited ClO radicals with O_3 or with Cl atoms, respectively. Burkholder et al. (1989), in a study of infrared line intensities of the ClO radical, present evidence in support of the second mechanism. In their experiments with excess Cl atoms, the vibrationally excited ClO radicals produced in the Cl+ O_3 reaction can react with Cl atoms to give Cl_2 and oxygen atoms which can then remove additional ClO radicals (Burkholder et al., 1989). These authors (Burkholder et al., 1989) point out the possibility for systematic error from assuming a 1:1 stoichiometry for $[ClO] : [O_3]_0$ when using the Cl+ O_3 reaction as a quantitative source of ClO radicals for kinetic and spectroscopic studies.

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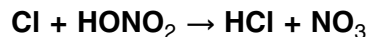
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III.A2.30



$$\Delta H^\circ = -4.8 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<5.0 \times 10^{-16}$	293	Zagogianni et al., 1987	DF-EPR
$<2.0 \times 10^{-16}$	298	Wine et al., 1988	PLP-AS (a)

Comments

(a) Pulsed laser photolysis of $\text{Cl}_2\text{-HNO}_3\text{-He}$ mixtures at 351 nm. NO_3 radical concentrations were monitored using long-path absorption spectroscopy. Experiments in which Cl atom concentrations were measured by resonance fluorescence were also carried out, but were less sensitive and resulted in higher upper limits to the rate coefficient, of $k < 1.3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and $k < 1.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 400 K.

Preferred Values

$k < 2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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Comments on Preferred Values

The preferred upper limit to the rate coefficient is that obtained by Wine et al. (1988), which receives support from the slightly higher value obtained by Zagogianni et al. (1987). Values from earlier studies (Leu and DeMore, 1976; Clark et al., 1982; 5 Kurylo et al., 1983) are well above the preferred upper limit to the rate coefficient k .

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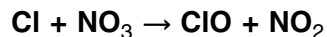
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III.A2.31



$$\Delta H^\circ = -60.2 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.6 \pm 0.5) \times 10^{-11}$	298	Mellouki et al., 1987	DF-EPR/MS
$(2.26 \pm 0.17) \times 10^{-11}$	298	Becker et al., 1991	DF-MS

Preferred Values

$k = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

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

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

Comments on Preferred Values

The preferred value at room temperature is based on the studies of Mellouki et al. (1987) and Becker et al. (1991). The results of these direct absolute rate studies are preferred over those of earlier relative rate studies (Cox et al., 1984; Burrows et al.,

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1985; Cox et al., 1987) in which NO_3 was monitored in the photolysis of $\text{Cl}_2\text{-ClONO}_2\text{-N}_2$ mixtures. The agreement among these earlier studies (Cox et al., 1984; Burrows et al., 1985; Cox et al., 1987) is not good and probably arises from complications in the chemistry of the systems used. This radical-radical reaction is expected to have a negligible temperature dependence, which is consistent with the results of Cox et al. (1987) over the temperature range 278 K to 338 K.

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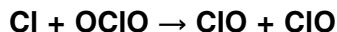
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III.A2.32



$$\Delta H^\circ = -12.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$>8.3 \times 10^{-13}$	298	Clyne and Coxon, 1968	DF-UVA
$(8.5 \pm 1.2) \times 10^{-12}$	~298	Basco and Dogra, 1971	FP-UVA
$(5.9 \pm 0.9) \times 10^{-11}$	298–588	Bemand et al., 1973	DF-RF/MS (a)
$3.0 \times 10^{-11} \exp(174/T)$	229–428	Toohey, 1988	DF-RF (b)
$(5.44 \pm 0.09) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$3.7 \times 10^{-10} \exp[-(3020 \pm 101)/T]$	338–365	Gritsan et al., 1975	(c)

Comments

(a) Discharge flow system with resonance fluorescence detection of Cl atom decay in excess OCIO and MS measurement of OCIO decay in excess Cl.

(b) The measured rate coefficients ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were: 229 K, $(6.28 \pm 0.21) \times 10^{-11}$; 247 K, $(6.12 \pm 0.20) \times 10^{-11}$; 268 K, $(5.6 \pm 0.30) \times 10^{-11}$; 298 K, $(5.44 \pm 0.09) \times 10^{-11}$; 367 K, $(4.84 \pm 0.24) \times 10^{-11}$; and 428 K, $(4.40 \pm 0.17) \times 10^{-11}$. A unit-weighted least-squares analysis of these data, using the Arrhenius expression, leads to $k = 3.0 \times 10^{-11} \exp(174/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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(c) Thermal decomposition of OCIO. Complex chemical system.

Preferred Values

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

$k = 3.2 \times 10^{-11} \exp(170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–430 K.

5 *Reliability*

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

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

Comments on Preferred Values

10 The data of Toohey (1988) agree well with the earlier study of Bemand et al. (1973) at 298 K, but show a small negative temperature dependence over a similar temperature range to that over which Bemand et al. (1973) saw little change in k . The preferred value is the average of the 298 K values from the two studies of Bemand et al. (1973) and Toohey (1988) and the temperature dependence of Toohey (1988) is accepted but with error limits covering the possibility that k is independent of temperature. The earlier data of Clyne and Coxon (1968) and Basco and Dogra (1971) are rejected following
15 the recommendation of Bemand et al. (1973).

References

Basco, N. and Dogra, S. K.: Proc. Roy. Soc. (London), A323, 417, 1971.

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Clyne, M. A. A. and Coxon, J. A.: Proc. Roy. Soc. (London), A303, 207, 1968.

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Gritsan, V. I., Panfilov, V. N., and Sukhanov, I. L.: Reaction Kinetics and Catalysis Letters, 2, 265, 1975.

Toohey, D. W.: Kinetic and Mechanistic Studies of Reactions of Bromine and Chlorine Species Important in the Earth's Stratosphere, Ph.D. Thesis, Harvard University,

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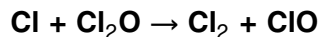
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III.A2.33



$$\Delta H^\circ = -96.9 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.33 \pm 0.54) \times 10^{-11}$	298	Ray et al., 1980	DF-MS
$(1.03 \pm 0.08) \times 10^{-10}$	298	Ray et al., 1980	DF-RF
$6.0 \times 10^{-11} \exp[(127 \pm 30)/T]$	233–373	Stevens and Anderson 1992	DF-RF
$(9.1 \pm 0.4) \times 10^{-11}$	298		

Preferred Values

$$k = 9.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 6.2 \times 10^{-11} \exp(130/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 230\text{--}380 \text{ K.}$$

Reliability

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

$$\Delta (E/R) = \pm 130 \text{ K.}$$

Comments on Preferred Values

The preferred room temperature value is the mean of the value reported by Stevens and Anderson (1992) and the values obtained by Ray et al. (1980) using two completely

independent techniques. This value is confirmed by the relative rate study of Burrows and Cox (1981). The much lower value reported earlier by Basco and Dogra (1971) has been rejected. The recommended temperature dependence is from Stevens and Anderson (1992). There is apparently no pressure dependence over the range 1 mbar to 1 bar (Ray et al., 1980; Stevens and Anderson, 1992; Burrows and Cox, 1981).

References

Basco, N. and Dogra, S. K.: Proc. Roy. Soc. London A, 323, 401, 1971.

Burrows, J. P. and Cox, R. A.: J. Chem. Soc. Faraday Trans., 1, 77, 2465, 1981.

Ray, G. W., Keyser, L. F., and Watson, R. T.: J. Phys. Chem., 84, 1674, 1980.

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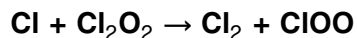
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III.A2.34



$$\Delta H^\circ = -151.4 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.00 \pm 0.02) \times 10^{-10}$	233	Cox and Hayman, 1988	(a)

Comments

(a) Static photolysis of $\text{Cl}_2\text{-Cl}_2\text{O-N}_2$ mixtures at 350 nm. The time dependence of $[\text{Cl}_2\text{O}_2]$ and $[\text{Cl}_2\text{O}]$ were monitored by photodiode array UV spectroscopy, yielding $k(\text{Cl}+\text{Cl}_2\text{O})/2k=0.54\pm 0.01$ at 233 K. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl}+\text{Cl}_2\text{O})=1.08\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 233 K (this evaluation).

Preferred Values

$k = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ independent of temperature over the range 230–300 K.

Reliability

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

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

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Comments on Preferred Values

The preferred values are based on the relative rate study of Cox and Hayman (1988) which is supported by the unpublished rate coefficient of Friedl (1991) of $(1.0 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The agreement of the room temperature value and that at 233 K along with the high value of k precludes a significant temperature dependence.

References

Cox, R. A. and Hayman, G. D.: Nature, 332, 796, 1988.

Friedl, R. R.: unpublished data, 1991.

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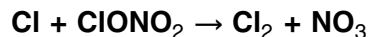
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III.A2.35



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

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$6.3 \times 10^{-12} \exp(150/T)$ $(1.04 \pm 0.16) \times 10^{-11}$	219–298 298	Margitan, 1983	FP-RF (a)
$7.3 \times 10^{-12} \exp(165/T)$ $(1.20 \pm 0.24) \times 10^{-11}$	220–296 296	Kurylo et al., 1983	FP-RF (b)
$6.0 \times 10^{-12} \exp[(140 \pm 30)/T]$ $(9.6 \pm 1.0) \times 10^{-12}$	195–298 298	Yokelson et al., 1995	PLP-RF/TDLS (c)
$(9.1 \pm 1.2) \times 10^{-12}$	298	Tyndall et al., 1997	PLP-RF

Comments

- (a) The O(³P) atom abstraction channel to give ClO+ClONO was shown to be unimportant based on results of experiments with added NO, in which Cl was not regenerated by the fast reaction ClO+NO → Cl+NO₂.
- (b) Supersedes earlier results from the same laboratory (Kurylo and Manning, 1977).
- (c) Decays of Cl atoms were measured by RF over the temperature range 195–354 K ($k=6.5 \times 10^{-12} \exp[(120 \pm 20)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and formation of NO₃ radicals were measured by tunable diode laser spectroscopy (TDLS) over the temper-

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ature range 200–298 K ($k=6.0 \times 10^{-12} \exp[(140 \pm 30)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The values cited in the table are the combined results of experiments using both detection systems for the temperature range 195–298 K.

Preferred Values

- 5 $k = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 6.2 \times 10^{-12} \exp(145/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 190–360 K.

Reliability

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

$\Delta (E/R) = \pm 50 \text{ K}$.

10 *Comments on Preferred Values*

The recommended Arrhenius equation is derived from the studies of Margitan (1983) and Yokelson et al. (1995), which are in excellent agreement. The data of Kurylo et al. (1983) and Tyndall et al. (1997) agree with the preferred values within the recommended uncertainty limits. Margitan (1983) has shown that the reaction proceeds
15 by Cl-atom abstraction rather than by O-atom abstraction and this was confirmed by Yokelson et al. (1995), who determined that more than 95% of the reaction formed Cl_2 and NO_3 at 298 K.

References

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20 Kurylo, M. J., Knable, G. L., and Murphy, J. L.: Chem. Phys. Lett., 95, 9, 1983.
Margitan, J. J.: J. Phys. Chem., 87, 674, 1983.

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Yokelson, R. J., Burkholder, J. B., Goldfarb, L., Fox, R. W., Gilles, M. K., and Ravishankara, A. R.: J. Phys. Chem., 99, 13 976, 1995.

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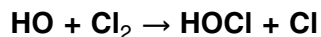
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III.A2.36



$$\Delta H^\circ = 6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

5

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.5 \pm 0.3) \times 10^{-14}$	298	Leu and Lin, 1979	DF-RF
$\sim 7.4 \times 10^{-14}$	298	Ravishankara et al., 1983	DF-RF
$(6.70 \pm 0.72) \times 10^{-14}$	298±3	Loewenstein and Anderson, 1984	DF-RF
$1.7 \times 10^{-12} \exp[-(911 \pm 373)/T]$	253–333	Boodaghians et al., 1987	DF-RF
$(6.8 \pm 1.0) \times 10^{-14}$	293±2		
$3.77 \times 10^{-12} \exp[-(1228 \pm 140)/T]$	231–354	Gilles et al., 1999	PLP-LIF
$(5.95 \pm 0.75) \times 10^{-14}$	298		

Preferred Values

$k = 6.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.6 \times 10^{-12} \exp(-1200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–360 K.

10

Reliability

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

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

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Comments on Preferred Values

The preferred values are based on the data of Loewenstein and Anderson (1984), Boodaghians et al. (1987) and Gilles et al. (1999), which are in good agreement concerning the room temperature rate coefficient. Because of the wider temperature range covered and more extensive study conducted, the preferred temperature dependence is that reported by Gilles et al. (1999) with the pre-exponential factor, A , being adjusted to fit the preferred 298 K rate coefficient. Loewenstein and Anderson (1984) determined that the exclusive products are HOCl+Cl.

References

Boodaghians, R. B., Hall, I. W., and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 2 83, 529, 1987.

Gilles, M. K., Burkholder, J. B., and Ravishankara, A. R.: Int. J. Chem. Kinet., 31, 417, 1999.

Leu, M. T. and Lin, C. L.: Geophys. Res. Lett., 6, 425, 1979.

Loewenstein, L. M. and Anderson, J. G.: J. Phys. Chem., 88, 6277, 1984.

Ravishankara, A. R., Eisele, F. L., and Wine, P. H.: J. Chem. Phys., 78, 1140, 1983.

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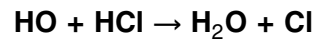
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III.A2.37



$$\Delta H^\circ = -65.4 \text{ kJ}\cdot\text{mol}^{-1}$$

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.4 \pm 0.7) \times 10^{-13}$	295	Takacs and Glass, 1973	DF-EPR
$4.1 \times 10^{-12} \exp[-(529 \pm 24)/T]$	220–480	Smith and Zellner, 1974	FP-RA
$(6.9 \pm 1) \times 10^{-13}$	298		
$2.0 \times 10^{-12} \exp[-(312 \pm 10)/T]$	224–440	Zahniser et al., 1974	DF-RF
$(6.7 \pm 0.4) \times 10^{-13}$	297		
$(6.6 \pm 1.7) \times 10^{-13}$	293	Hack et al., 1977	DF-EPR (a)
$3.3 \times 10^{-12} \exp[-(472 \pm 40)/T]$	250–402	Ravishankara et al., 1977	FP-RF
$(6.6 \pm 0.4) \times 10^{-13}$	298		
$(6.66 \pm 0.52) \times 10^{-13}$	300	Husain et al., 1981	FP-RF
$(6.8 \pm 0.25) \times 10^{-13}$	298±4	Cannon et al., 1984	FP-LIF
$2.1 \times 10^{-12} \exp[-(285 \pm 40)/T]$	258–334	Keyser, 1984	DF-RF
$(7.9 \pm 0.4) \times 10^{-13}$	295±2		
$4.6 \times 10^{-12} \exp[-(500 \pm 60)/T]$	240–295	Molina et al., 1984	PLP/FP-RF
$(8.5 \pm 1.5) \times 10^{-13}$	295		
$2.94 \times 10^{-12} \exp[-(446 \pm 32)/T]$	300–700	Husain et al., 1984	FP-RF
$(6.7 \pm 0.46) \times 10^{-13}$	300		
$2.4 \times 10^{-12} \exp[-(327 \pm 28)/T]$	240–363	Ravishankara et al., 1985	FP-RF/PLP-RF/
$(8.01 \pm 0.44) \times 10^{-13}$	298		PLP-LIF (b)
$(7.8 \pm 0.3) \times 10^{-13}$	298	Sharkey and Smith, 1993	PLP-LIF
$(5.4 \pm 0.25) \times 10^{-13}$	216		
$(5.6 \pm 0.45) \times 10^{-13}$	178		
$(5.2 \pm 0.3) \times 10^{-13}$	138		
$3.28 \times 10^{-17} T^{1.66} \exp(184/T)$	200–400	Battin-Leclerc et al., 1999	PLP-LIF (c)
$(7.96 \pm 0.60) \times 10^{-13}$	298		

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- (a) Rate coefficients also measured at 435 K and 567 K of $8.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $1.25 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively.
- (b) Rate coefficients measured over the temperature range 240–1055 K. The Arrhenius plot of the rate coefficients measured over this extended temperature range is curved, with $k = 4.5 \times 10^{-17} T^{1.65} \exp(112/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Ravishankara et al., 1985).
- (c) Over the limited temperature range 200–298 K, the data were also fit to the Arrhenius expression, with $k = 1.7 \times 10^{-12} \exp[-(225 \pm 20)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (note that the publication (Battin-Leclerc et al., 1999) gives a pre-exponential factor in the Arrhenius expression of $1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Rate coefficients were also measured for the reactions of the HO radical with DCI (252–387 K) and for the reactions of the DO radical with HCl (213–372 K) and DCI (213–401 K).

Preferred Values

$k = 8.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.8 \times 10^{-12} \exp(-240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

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

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

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The studies of Keyser (1984), Molina et al. (1984), Ravishankara et al. (1985) and Battin-Leclerc et al. (1999), which paid careful attention to the HCl present in the experiments, all show room temperature values higher by about 20% to 25% than most other studies (Takacs and Glass, 1973; Smith and Zellner, 1974; Zahniser et al., 1974; Hack et al., 1977; Ravishankara et al., 1977; Husain et al., 1981, 1984; Cannon et al., 1984). Ravishankara et al. (1985) showed that HCl losses can be a problem, leading to erroneously low measured rate coefficients, and this is a plausible cause of these discrepancies. The rate coefficients obtained in the recent and extensive study of Battin-Leclerc et al. (1999) are in good agreement with the data of Keyser (1984), Molina et al. (1984) and Ravishankara et al. (1985). The rate coefficients measured by Battin-Leclerc et al. (1999) at temperatures <240 K lead to a curved Arrhenius plot, in agreement with the previous study of Ravishankara et al. (1985) which extended to 1055 K and in which non-Arrhenius behavior was also observed. The preferred temperature-dependent expression for the range 200–300 K is obtained by a linear least-squares fit to the ≤ 299 K data from the studies of Keyser (1984), Molina et al. (1984), Ravishankara et al. (1985) and Battin-Leclerc et al. (1999). Over more extended temperature ranges the three-parameter expression obtained by Battin-Leclerc et al. (1999) should be used. Results of the low temperature study of Sharkey and Smith (1993) are in good agreement with the recommended Arrhenius expression down to 216 K, but are (as expected due to the non-Arrhenius behavior) significantly higher at 178 K and 138 K.

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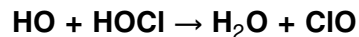
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III.A2.38



$$\Delta H^\circ = -99.4 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.7\text{--}9.5) \times 10^{-13}$	298	Ennis and Birks, 1988	DF-RF/MS (a)

Comments

(a) HO radical decays in the presence of excess HOCl were monitored by resonance fluorescence. HOCl concentrations were measured by MS. The effects of the presence of Cl_2O and Cl_2 impurities in the HOCl and the occurrence of secondary reactions were investigated through computer modeling, and the lower and upper limits to the rate coefficient k cited in the table obtained.

Preferred Values

$$k = 5.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

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

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Comments on Preferred Values

The only reported experimental value (Ennis and Birks, 1988) has a large uncertainty, and the preferred value is based on the mid-range value of $5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K from this study.

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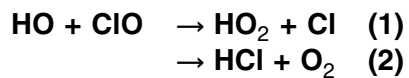
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III.A2.39



$$\Delta H^\circ(1) = -2.9 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -231 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.1 \pm 1.3) \times 10^{-12}$	298	Leu and Lin, 1979	DF-RF
$(1.17 \pm 0.33) \times 10^{-11}$	248–335	Ravishankara et al., 1983	DF-RF
$(1.19 \pm 0.09) \times 10^{-11}$	243–298	Burrows et al., 1984	DF-RF (a)
$8.0 \times 10^{-12} \exp[(235 \pm 46)/T]$	219–373	Hills and Howard, 1984	DF-LMR (b)
$(1.75 \pm 0.31) \times 10^{-11}$	298		
$(1.94 \pm 0.38) \times 10^{-11}$	298	Poulet et al., 1986	DF-LIF (c)
$5.5 \times 10^{-12} \exp[(292 \pm 72)/T]$	205–298	Lipson et al., 1997	DF-CIMS
$(1.46 \pm 0.23) \times 10^{-11}$	298		
$k_2 = 1.7 \times 10^{-13} \exp[(363 \pm 50)/T]$	210–298	Lipson et al., 1997	DF-CIMS (d)
$k_2 = 5.7 \times 10^{-13}$	298		
$8.9 \times 10^{-12} \exp[(295 \pm 95)/T]$	234–356	Kegley-Owen et al., 1999	DF (e)
$(2.44 \pm 0.63) \times 10^{-11}$	298		
$k_2 = 3.2 \times 10^{-13} \exp[(325 \pm 60)/T]$	207–298	Lipson et al., 1999	F-CIMS (f)
$k_2 = (9.5 \pm 1.6) \times 10^{-13}$	298		
$6.7 \times 10^{-12} \exp[(360 \pm 90)/T]$	230–360	Bedjanian et al., 2001	DF-MS (g)
$(2.2 \pm 0.4) \times 10^{-11}$	298		
$k_2 = 9.7 \times 10^{-14} \exp[(600 \pm 120)/T]$	230–320		
$k_2 = (7.3 \pm 2.2) \times 10^{-13}$	298		
$7.2 \times 10^{-12} \exp[(333 \pm 70)/T]$	218–298	Wang and Keyser, 2001	DF-RF/UVA (h)
$(2.22 \pm 0.33) \times 10^{-11}$	298		
$k_2 = (1.25 \pm 0.45) \times 10^{-12}$	298	Tyndall et al., 2002	FP-IR (i)
<i>Branching Ratios</i>			
$k_2/k = 0.05 \pm 0.02$	298	Lipson et al., 1997	DF-CIMS (j)
$k_2/k = 0.06 \pm 0.02$	210		
$k_2/k = 0.090 \pm 0.048$	218–298	Wang and Keyser, 2001	DF-RF/IR/UVA (h,k)

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Comments

- (a) Rate coefficient ratio of $k_1/k=0.85\pm 0.07$, independent of temperature over the range 243–298 K, was determined from measurement of HO₂ radical concentrations (after conversion to HO radicals by reaction with NO).
- (b) The rate coefficient ratio, k_1/k , was measured to be $k_1/k=0.86\pm 0.14$ at 293 K from measurement of the HO₂ radical concentrations by LMR.
- (c) The rate coefficient ratio, k_1/k , was measured to be 0.98 ± 0.12 at 298 K from MS detection of HCl.
- (d) Measurements of the DCI product by CIMS in experiments using DO radicals. The overall rate coefficient measured for reaction of DO radicals with ClO radicals was $k=4.2\times 10^{-12} \exp[(280\pm 114)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200 K to 298 K, a factor of 1.35–1.4 lower than the rate coefficient for the HO radical reaction.
- (e) HO radicals were generated by pulsed laser photolysis of O₃ (or ClO) at 248 nm and monitored by LIF. ClO radicals were generated by reaction of Cl atoms (produced by a microwave discharge in Cl₂-He mixtures) with O₃, and monitored by UV/visible absorption.
- (f) Turbulent flow reactor operated at total pressures of 125 mbar to 270 mbar. The measurements of the rate coefficients k_2 were combined with the overall rate coefficient $k=5.5\times 10^{-12} \exp(292/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ previously determined by the same research group (Lipson et al., 1997) to derive the branching ratio $k_2/k=0.07\pm 0.03$, independent of temperature (207–298 K) and total pressure (125–270 mbar).
- (g) ClO generated from Cl+O₃ (following discharge of Cl₂ or F+Cl₂). HO was generated from H+NO₂ (following discharge of H₂). ClO concentrations were measured

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directly at the parent peak. HO measured as HOBr⁺, following titration with Br₂. Experiments carried out at 1 Torr under pseudo-first order conditions with ClO in excess. Direct measurement of k_2 from observed HCl formation is consistent with $k_2/k = 0.035 \pm 0.010$ over the temperature range 230–320 K.

(h) ClO generated from Cl+O₃ (following discharge of Cl₂). HO was generated either from F+H₂O (following discharge of F₂) or from H+NO₂ (following discharge of H₂). ClO and HO concentrations measured by UV absorption and RF, respectively. Experiments carried out at 1.3 mbar under pseudo-first order conditions with ClO in excess.

(i) ClO and HO generated from the 308 nm laser photolysis of Cl₂-O₃-H₂O-He mixtures at ~40–55 mbar. Initial concentrations of ClO and HO calculated from laser fluence and precursor concentrations. HCl production determined using time-resolved tunable diode laser spectroscopy. k_2 determined from simulation of the results of experiments performed with a range of starting conditions.

(j) From the rate coefficients k_2 and k for the DO radical reaction.

(k) HCl measured using long-path tunable diode laser spectroscopy.

Preferred Values

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

$k = 7.3 \times 10^{-12} \exp(300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–380 K.

$k_2/k = 0.06$, independent of temperature over the range 200–300 K.

Reliability

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

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

$\Delta(k_2/k) = \pm 0.04$ over the temperature range 200–300 K.

Comments on Preferred Values

The preferred value of k at 298 K is an average of the values reported by Hills and Howard (1984), Poulet et al. (1986), Lipson et al. (1997), Kegley-Owen et al. (1999), Bedjanian et al. (2001) and Wang and Keyser (2001). The preferred Arrhenius expression is based on the mean of the E/R values from the temperature dependence studies of Hills and Howard (1984), Lipson et al. (1997), Kegley-Owen et al. (1999), Bedjanian et al. (2001) and Wang and Keyser (2001), combined with a pre-exponential factor adjusted to give the preferred value of k at 298 K. These studies are generally in good agreement, as reflected in the uncertainties assigned to k and E/R . Values of the branching ratio, k_2/k , derived from both direct measurements of k_2 and k (Lipson et al., 1997; Bedjanian et al., 2001) and from measurements of the branching ratio itself (Wang and Keyser, 2001), yield values lying in the range 0.035–0.09. The temperature independent preferred value of k_2/k is based on the mean of these values, with the assigned uncertainty encompassing the extremes of the reported measurements.

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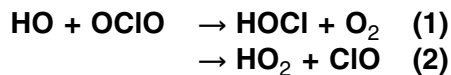
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III.A2.40



$$\Delta H^\circ(1) = -210 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -15.6 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.50 \times 10^{-13} \exp[(804 \pm 114)/T]$	293–473	Poulet et al., 1986	DF-LIF/EPR (a)
$(7.2 \pm 0.5) \times 10^{-12}$	293		

Comments

(a) HOCl was observed as a reaction product, using MS, and its concentration determined using the $\text{HO}+\text{Cl}_2 \rightarrow \text{HOCl}+\text{Cl}$ reaction as a calibration source of HOCl. Computer simulation of the reaction system indicated that HOCl is formed primarily in the HO+OCIO reaction [channel (1)] and not as a result of secondary reactions of the HO₂ radical with ClO, with $k_1/k \geq 0.80$ at room temperature.

Preferred Values

$$k = 6.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 4.5 \times 10^{-13} \exp(800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 290\text{--}480 \text{ K.}$$

$$k_1/k = 1.0$$

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Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.

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

$\Delta \log (k_1/k) = \pm 0.2$ at 298 K.

5 *Comments on Preferred Values*

The preferred values are based on the only experimental study of Poulet et al. (1986) using a discharge flow system at ~ 1.3 mbar, with EPR and LIF detection of HO radical decay and molecular beam mass spectrometry detection of the product HOCl. Indication of curvature in the Arrhenius plot dictates caution in extrapolation beyond the experimental range.

10 Xu et al. (2003) have recently reported ab initio molecular orbital and variational RRKM theory calculations of the rate coefficient and product channels. The results provide support for both the magnitude of the rate coefficient, and the dominance of channel (1), as reported by Poulet et al. (1986) at 1.3 mbar. Channel (2) is predicted to gain importance at elevated temperatures, and a pressure-dependent association channel to form HOClO₂ is predicted to account for $\sim 20\%$ of the reaction at 100 Torr and 300 K, and to be the major channel at atmospheric pressure. Experimental studies at higher pressures are required to investigate this.

References

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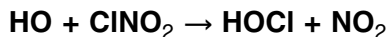
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III.A2.41



$$\Delta H^\circ = -94 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.5 \pm 0.7) \times 10^{-14}$	298	Ganske et al., 1991	DF-RF (a)
$2.4 \times 10^{-12} \exp[-(1250 \pm 155)/T]$	259–348	Ganske et al., 1992	DF-RF/MS (a)
$(3.6 \pm 0.2) \times 10^{-14}$	298		

Comments

(a) Flow tube at 1.35 mbar. HO formed from $\text{H} + \text{NO}_2$ and detected by resonance fluorescence. Product analysis using mass spectrometry revealed HOCl to be the sole chlorine-containing product.

Preferred Values

$k = 3.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.4 \times 10^{-12} \exp(-1250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–350 K.

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Reliability

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

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

Comments on Preferred Values

5 The preferred values are based on the results of the temperature-dependent study of Ganske et al. (1992). Mass spectrometric measurements (Ganske et al., 1991, 1992) showed HOCl to be the sole chlorine-containing product, with no evidence for production of HONO₂ or Cl₂, thereby showing that the only reaction pathway is that yielding HOCl+NO₂.

10 References

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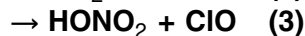
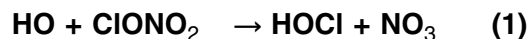
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III.A2.42



$$\Delta H^\circ(1) = -64 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = 10 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(3) = -93.6 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.7 \pm 0.2) \times 10^{-13}$	245	Ravishankara et al., 1977	FP-RF
$1.19 \times 10^{-12} \exp[-(333 \pm 22)/T]$	246–387	Zahniser et al., 1977	DF-RF
$(3.93 \pm 0.11) \times 10^{-13}$	295		

Preferred Values

$$k = 4.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$10 \quad k = 1.2 \times 10^{-12} \exp(-330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}390 \text{ K.}$$

Reliability

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

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

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Comments on Preferred Values

The results of the only two reported studies of Ravishankara et al. (1977) and Zahniser et al. (1977) are in good agreement at 245 K (within 25%), considering the difficulties associated with handling ClONO₂. The preferred value is based on the temperature-dependent study of Zahniser et al. (1977). Neither study reported any data concerning the reaction products.

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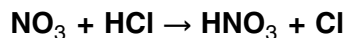
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III.A2.43



$$\Delta H^\circ = 4.8 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<7 \times 10^{-18}$	298	Cantrell et al., 1987	(a)
$\leq 5 \times 10^{-17}$	298	Mellouki et al., 1989	DF-EPR (b)
$<2.4 \times 10^{-17}$	298	Canosa-Mas et al., 1989	DF-A (c)

Comments

- (a) NO_3 radical concentrations were derived from the measured NO_2 and N_2O_5 concentrations in N_2O_5 - NO_2 - NO_3 - HCl -air mixtures, using the equilibrium constant of Graham and Johnston (1978). The upper limit to the rate coefficient cited above was derived from computer fits of the time-concentration data for reactants and products monitored by FTIR absorption spectrometry.
- (b) The upper limit to the rate coefficient cited above was derived from fitting the measured upper limit to the ClO radical concentration (determined by EPR after conversion to Cl atoms) to a complex mechanism.
- (c) No reaction was observed at room temperature, leading to the upper limit to the rate coefficient cited above. At higher temperatures (333 K to 473 K), rate coefficients derived from fitting to a complex mechanism yielded the Arrhenius expression of $k = 4 \times 10^{-12} \exp(-3330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred Values

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

Comments on Preferred Values

The preferred value is the upper limit to the rate coefficient reported by Mellouki et al. (1989) in a study using the discharge flow-EPR technique. Somewhat lower upper limits have been reported by Cantrell et al. (1987) and by Canosa-Mas et al. (1989). Canosa-Mas et al. (1989) also reported Arrhenius parameters at higher temperatures (over the range 333 K to 473 K). The preferred value indicates that this reaction is not important in the chemistry of the atmosphere.

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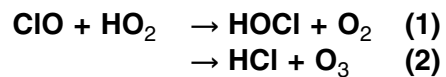
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III.A2.44



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

$$\Delta H^\circ(2) = -65.8 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.8 \pm 0.7) \times 10^{-12}$	298	Reimann and Kaufman, 1978	DF-RF
$3.3 \times 10^{-11} \exp(850/T) +$ $4.5 \times 10^{-12} (T/300)^{-3.7}$	235–393	Stimpfle et al., 1979	DF-LMR
$(6.43 \pm 0.96) \times 10^{-12}$	298		
$(4.5 \pm 0.9) \times 10^{-12}$	298	Leck et al., 1980	DF-MS
$(5.4_{-2}^{+4}) \times 10^{-12}$	300	Burrows and Cox, 1981	MM-UVA
$(6.2 \pm 1.5) \times 10^{-12}$	308	Cattell and Cox, 1986	MM-UVA (a)
$2.84 \times 10^{-12} \exp[(312 \pm 60)/T]$	203–364	Nickolaisen et al., 2000	FP-UVA (b)
$(7.79 \pm 0.83) \times 10^{-12}$	299		(c)
$(8.26 \pm 1.38) \times 10^{-12}$	299		(d)
$7.1 \times 10^{-12} \exp[(-16 \pm 17)/T]$	215–298	Knight et al., 2000	DF-MS (e)
$(7.1 \pm 1.8) \times 10^{-12}$	294		
<i>Branching Ratios</i>			
$k_2/k \leq 0.02$	298	Leck et al., 2000	(f)
$k_2/k \leq 0.015$	298	Leu, 1980	(f)
$k_2/k \leq 0.03$	248		
$k_2/k \leq 0.003$	298	Burrows and Cox, 1981	(g)
$k_1/k \geq 0.95$	210–300	Finkbeiner et al., 1995	(h)
$k_2/k = 0.05 \pm 0.02$	210		
$k_2/k = 0.02 \pm 0.01$	240		
$k_2/k \leq 0.01$	215–298	Knight et al., 2000	(f)

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- (a) k independent of pressure over the range 65–1000 mbar.
- (b) k independent of pressure over the range 65–930 mbar. Two chemical systems employed to generate ClO and HO₂: (i) the photolysis of Cl₂-Cl₂O-CH₃OH-O₂-N₂ mixtures, and (ii) the photolysis of F₂-H₂-O₂-Cl₂O-N₂ mixtures. The latter system consistently yielded slightly higher values of k , although differences are well within error limits of each system. Unpublished results (Laszlo et al.) from the same laboratory using DF-MS at 1 Torr are also cited. The results give a near-zero temperature dependence over the range 233–380 K ($E/R=72\pm 42$ K), and a value of k about a factor of 2 lower at 298 K compared with the FP-UVA measurement.
- (c) Cl₂-Cl₂O-CH₃OH-O₂-N₂ system.
- (d) F₂-H₂-O₂-Cl₂O-N₂ system.
- (e) k measured in 1.4–2.2 mbar He. ClO and HO₂ generated from five combinations of precursor reagents: (i) CH₃OH-Cl₂O, (ii) CH₃OH-OCIO, (iii) HCHO-Cl₂O, (iv) HCHO-OCIO, and (v) H₂O₂-OCIO. Systems yielded consistent results. Additional experiments performed with related chemical systems involving presence of O₃, generated higher values of k , described by the expression $(6.6\pm 0.8)\times 10^{-12} \exp[(85\pm 18)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, over the temperature range 223–333 K. This was attributed to inefficient quenching at 1.3 mbar of the vibrationally excited ClO generated from the Cl+O₃ reaction.
- (f) DF-MS detection of O₃.
- (g) MM-CL detection of O₃.

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(h) Flow system with steady-state photolysis (310 nm to 400 nm) of Cl₂-H₂-Cl₂O-O₂-Ar mixtures at a total pressure of 910 mbar. HOCl and O₃ products were monitored by matrix-isolation FTIR spectroscopy.

Preferred Values

- 5 $k = 6.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.2 \times 10^{-12} \exp(340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–300 K.

Reliability

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

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

10 *Comments on Preferred Values*

The reported studies have been carried out over a range of temperatures and pressures, using a variety of techniques. The room temperature values of k cover a range of more than a factor of two. Systematic studies of the pressure dependence (Cattell and Cox, 1986; Nickolaisen et al., 2000) show no significant variation above 65 mbar, although the average of the published low pressure discharge flow measurements is slightly lower than the average of the higher pressure measurements. The recent studies of the temperature dependence (Nickolaisen et al., 2000; Knight et al., 2000) disagree with the previously reported (Stimpfle et al., 1979) strong negative temperature dependence at temperatures below 298 K, and the associated non-linear Arrhenius behaviour. However, there is also substantial disagreement between the recent studies, which yield values of E/R of -312 K (Nickolaisen et al., 2000) and 16 K (Knight et al., 2000).

The preferred value at 298 K is based on the average of the room temperature data of Stimpfle et al. (1979), Cattell and Cox (1986), Nickolaisen et al. (2000) and

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Knight et al. (2000). The preferred value of E/R is based on the average of the three temperature dependence studies, using Stimpfle et al. (1979) data for $T \leq 298$ K (for which $E/R = -709$ K). The uncertainties in k at 298 K and E/R reflect the range of reported values.

5 All of the available data suggest that channel (1) is the dominant, if not sole, pathway over the temperature range of the preferred values. With the exception of the matrix-isolation results of Finkbeiner et al. (1995) no evidence for channel (2) has been reported. Recent theoretical studies (Nickolaisen et al., 2000; Kaltsoyannis and Rowley, 2002) conclude that the contribution of channel (2) is essentially zero.

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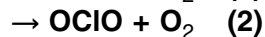
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III.A2.45



$$\Delta H^\circ(1) = -146.8 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -149.7 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_2 < 1 \times 10^{-18}$	298	DeMore et al., 1975	DF-MS
$k_2 < 1 \times 10^{-18}$	298	Wongdontri-Stuper et al., 1979	FP-UVA (a)
$k_1 < 1.3 \times 10^{-17}$	233	Stevens and Anderson, 1990	(b)
$k_1 < 1.4 \times 10^{-17}$	298		
$k_1 = (4.0 \pm 2.0) \times 10^{-16}$	413		

Comments

(a) Flash photolysis of $\text{Cl}_2\text{-O}_3$ mixtures. Upper limit to the rate coefficient obtained expected to really refer to k_2 (Stevens and Anderson, 1990).

10 (a) Discharge flow system. Reaction channel (1) was followed by monitoring ClO produced from the thermal decomposition of the product ClOO in the presence of O_3 . The product ClO was distinguished from the reactant ClO through isotopic labelling.

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Preferred Values

$k_1 < 1.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2 < 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

5 The preferred upper limit for k_1 is based on the results of the study of Stevens and Anderson (1990). The preferred upper limit for k_2 is based on the data of DeMore et al. (1975) and Wongdontri-Stuper et al. (1979). The upper limit of Stevens and Anderson (1990) at room temperature can be combined with their measured rate coefficient at 413 K to derive $A_1 = 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $E_1/R > 3600 \text{ K}$. For k_2 one can
10 estimate $A_2 = 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and derive $E_2/R > 4000 \text{ K}$.

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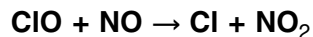
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$$\Delta H^\circ = -37.4 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.7 \pm 0.2) \times 10^{-11}$	298	Clyne and Watson, 1974	DF-MS
$5.72 \times 10^{-12} \exp[(296 \pm 20)/T]$	227–415	Leu and DeMore, 1978	DF-MS
$(1.53 \pm 0.11) \times 10^{-11}$	299		
$(1.61 \pm 0.16) \times 10^{-11}$	295	Clyne and MacRobert, 1980	DF-MS
$(1.72 \pm 0.20) \times 10^{-11}$	298	Ray and Watson, 1981	DF-MS
$7.1 \times 10^{-12} \exp[(270 \pm 50)/T]$	202–393	Lee et al., 1982	DF-LMR
$(1.84 \pm 0.03) \times 10^{-11}$	297		

Preferred Values

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

$$k = 6.2 \times 10^{-12} \exp(295/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}420 \text{ K.}$$

Reliability

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

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

Comments on Preferred Values

The room temperature rate coefficients reported by Clyne and Watson (1974), Leu and DeMore (1978), Clyne and MacRobert (1980), Ray and Watson (1981) and Lee et al. (1982) are in good agreement and are ~30% lower than the value reported by Zahniser and Kaufman (1977) from a competitive study. The preferred values are derived from a least-squares fit to the data reported by Clyne and Watson (1974), Leu and DeMore (1978), Clyne and MacRobert (1980), Ray and Watson (1981) and Lee et al. (1982).

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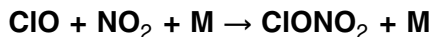
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$$\Delta H^\circ = -111.9 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.40 \pm 0.66) \times 10^{-33} \exp(1087/T) [\text{N}_2]$	250–356	Birks et al., 1977	DF-MS (a)
$(1.52 \pm 0.23) \times 10^{-31} (T/300)^{-3.15} [\text{N}_2]$	251–365	Zahniser et al., 1977	DF-RF (b)
$(3.69 \pm 0.24) \times 10^{-33} \exp(1150/T) [\text{N}_2]$		Leu et al., 1977	DF-MS (c)
$4.3 \times 10^{-33} \exp[(1085 \pm 86)/T] [\text{N}_2]$	274–339	Cox and Lewis, 1979	(d)
$(1.5 \pm 0.12) \times 10^{-31} [\text{N}_2]$	298	Molina et al., 1980	PLP-UVA (e)
$(1.5 \pm 0.2) \times 10^{-31} [\text{N}_2]$	298	Dasch et al., 1981	PLP-UVA (f)
$2.8 \times 10^{-33} \exp(1090/T) [\text{He}]$	250–387	Lee et al., 1982	DF-LMR
$3.5 \times 10^{-33} \exp(1180/T) [\text{O}_2]$	250–416		(g)
$2.09 \times 10^{-31} [\text{N}_2]$	297		
$(1.8 \pm 0.4) \times 10^{-31} [\text{N}_2]$	270–295	Cox et al., 1984	(h)
$(1.6 \pm 0.2) \times 10^{-31} (T/300)^{-3.0} [\text{N}_2]$	264–343	Handwerk and Zellner, 1984	FP-UVA (i)
$(1.40 \pm 0.07) \times 10^{-31} [\text{N}_2]$	298	Wallington and Cox, 1986	(j)
$(1.8 \pm 0.3) \times 10^{-31} (T/300)^{-3.4} [\text{air}]$	213–298	Percival et al., 1997	(k)

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- (a) Pressure range 1.3–7 mbar.
- (b) Resonance fluorescence of Cl after conversion of ClO into Cl. Pressure range 1.4–9 mbar. Measurement in N₂ only at 300 K, temperature coefficient taken from measurements in He.
- (c) Pressure range 1.3–8 mbar.
- (d) Modulated photolysis with UV absorption detection of ClO radicals. The pressure range studied was 33–815 mbar. Small deviations from third-order kinetics were observed near 1 bar.
- (e) The ClO radical decay was monitored. FTIR spectroscopy was also used to monitor the reaction products.
- (f) ClO radicals were generated from Cl₂O and monitored at 258.2 nm. The pressure range was 27–800 mbar.
- (g) Detection of ClO($X^2\Pi_{3/2}$, $\nu=0$) with an optically pumped spectrometer. Measurements were carried out at pressures over the range 0.8–8.8 mbar.
- (h) Modulated photolysis of Cl₂-Cl₂O-NO₂-N₂ mixtures. ClONO₂ formation was followed by diode laser spectroscopy. This study ruled out the formation of isomers other than ClONO₂.
- (i) The pressure range was 23–1052 mbar, with experiments being conducted at 264 K, 298 K and 343 K.
- (j) Modulated photolysis of OCIO-NO₂-N₂ mixtures with detection of ClO radicals by UV absorption.

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(k) Turbulent flow measurements at 213 K and 298 K with high pressure chemical ionization mass spectrometry over the pressure range 200–790 mbar. The falloff extrapolation used $F_c=0.6$, in agreement with earlier data.

Preferred Values

5 $k_0 = 1.6 \times 10^{-31} (T/300)^{-3.4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–350 K.

Reliability

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

$\Delta n = \pm 1$.

10 *Comments on Preferred Values*

There is excellent agreement between the various studies of this reaction in the falloff region close to the low pressure limit (Birks et al., 1977; Zahniser et al., 1977; Leu et al., 1977; Cox and Lewis, 1979; Molina et al., 1980; Dasch et al., 1981; Lee et al., 1982; Cox et al., 1984; Handwerk and Zellner, 1984; Wallington and Cox, 1986; Percival et al., 1997).

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High-pressure rate coefficients

Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3-6) \times 10^{-12}$	298	Dasch et al., 1981	PLP-UVA (a)
$(1.2_{-0.6}^{+1.2}) \times 10^{-11}$	264-343	Handwerk and Zellner, 1984	FP-UVA (b)
$(1.5 \pm 0.7) \times 10^{-11} (T/300)^{-1.9}$	213-298	Percival et al., 1997	(c)

Comments

(a) See comment (f) for k_0 . The extrapolation to k_{∞} is very uncertain, and the value of F_c was unspecified.

(b) See comment (i) for k_0 . The extrapolation to k_{∞} is very uncertain. The reported value of k_{∞} was based on theoretical predictions. Using the reported values of k_0 and k_{∞} and $F_c=0.55, 0.50$ and 0.45 at 264 K, 298 K and 343 K, respectively, falloff curves were obtained which are in good agreement with the majority of the available data.

(c) See comment (k) for k_0 . The falloff extrapolation was carried out with $F_c=0.6$, independent of temperature.

Preferred Values

$k_{\infty} = 7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–350 K.

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Reliability

$\Delta \log k_{\infty} = \pm 0.3$ over the temperature range 250–350 K.

Comments on Preferred Values

Because there are no direct measurements of k at pressures much above 1 bar, k_{∞} cannot be established with certainty. There are two alternatives for a representation of the rate data at pressures up to 1 bar. One may use the values chosen by Percival et al. (1997) with $F_c=0.6$ and a temperature dependent k_{∞} such as given in the table. Alternatively, one may follow our policy of choosing a more reasonable F_c such as recommended by Cobos and Troe (2003) and then fit k_{∞} . Using $F_c=0.4$ such as recommended also for $\text{HO}+\text{NO}_2 (+\text{M}) \rightarrow \text{HONO}_2 (+\text{M})$, the rate data in the falloff range below 1 bar from Percival et al. (1997) are well reproduced with a temperature independent $k_{\infty}=(7\pm 2)\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Because a value for F_c smaller than 0.6 appears theoretically much more justified, we here adopt the second alternative. However, we emphasize that the two alternatives work equally well for the representation of data below 1 bar.

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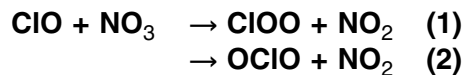
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III.A2.48



$$\Delta H^\circ(1) = -44.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -47.5 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.0 \pm 1.6) \times 10^{-13}$	296	Cox et al., 1984	MM-A
$1.6 \times 10^{-12} \exp[-(420 \pm 200)/T]$	278–338	Cox et al., 1987	MM-A (a)
4.0×10^{-13}	300		
$(5.0 \pm 1.4) \times 10^{-13}$	210–353	Biggs et al., 1991	DF-A/MS (b)
$(4.61 \pm 0.60) \times 10^{-13}$	300	Kukui et al., 1994	DF-MS (c)
$k_2 = (1.46 \pm 0.40) \times 10^{-13}$	300		
<i>Branching Ratios</i>			
$k_1/k = 0.73$	300	Cox et al., 1987	MM-A (a)
$k_2/k = 0.14 \pm 0.13$	353	Biggs et al., 1991	DF-A/MS (b)
$k_2/k = 0.20 \pm 0.10$	297		
$k_2/k = 0.035 \pm 0.050$	216		

Comments

(a) Derived from computer analysis of the NO_3 radical and ClO radical profiles.

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(b) Pseudo-first-order decay of NO_3 in excess ClO was determined by optical absorption at 662 nm, using a cross-section of $1.7 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. Product branching ratios were measured with a quadrupole mass spectrometer.

(c) Rate coefficients k were obtained from the first-order NO_3 radical decays in the presence of excess ClO radicals and O_3 . Rate coefficients k_2 were obtained from the decays of ClO radicals in the presence of excess NO_3 radicals, with ClOO radicals formed in channel (1) reforming ClO radicals by the reactions $\text{ClOO} \rightarrow \text{Cl} + \text{O}_2$ and $\text{Cl} + \text{NO}_3 \rightarrow \text{ClO} + \text{NO}_2$. This study (Kukui et al., 1994) supersedes the earlier study of Becker et al. (1991) from the same laboratory.

Preferred Values

$k = 4.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 210–360 K.

$k_2 = 1.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

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

$\Delta \log k_2 = \pm 0.3$ at 298 K.

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

Comments on Preferred Values

The preferred 298 K value is based on the results of Kukui et al. (1994) which are in agreement with the data of Cox et al. (1984, 1987) and Biggs et al. (1991). The results of Cox et al. (1987) are consistent with those of Biggs et al. (1991) who reported that the rate coefficient is independent of temperature over the range 210 K to 353 K. The two direct measurements of the branching ratio k_2/k , of 0.20 ± 0.10 at 297 K (Biggs et

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al., 1991) and 0.32 ± 0.1 at 300 K (Kukui et al., 1994), are in agreement that channel (1) dominates, and the preferred value of k_2 is based on the results of these two studies (Biggs et al., 1991; Kukui et al., 1994). From a study of the OCIO-NO₃ system, Friedl et al. (1992) conclude that at 220 K and 298 K the major reaction channel is channel (1),
5 in agreement with the conclusions of Cox et al. (1987), Biggs et al. (1991) and Kukui et al. (1994).

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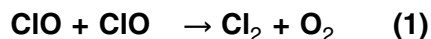
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$$\Delta H^\circ(1) = -203.2 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = 15.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(3) = 12.7 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = 1.01 \times 10^{-12} \exp[-(1590 \pm 100)/T]$	260–390	Nickolaisen et al., 1994	(a)
$k_2 = 2.98 \times 10^{-11} \exp[-(2450 \pm 330)/T]$	260–390		
$k_3 = 3.50 \times 10^{-13} \exp[-(1370 \pm 150)/T]$	260–390		
<i>Branching Ratios</i>			
$k_1/k = 0.39 \pm 0.06$	298	Horowitz et al., 1994	(b)
$k_2/k = 0.41 \pm 0.06$	298		
$k_3/k = 0.20 \pm 0.03$	298		
$k_3/k_2 = 0.27 \exp[(220 \pm 100)/T]$	285–331		

Comments

- 10 (a) Flash photolysis-long pathlength UV absorption technique. Cl_2 - Cl_2O mixtures were photolyzed at wavelengths longer than 300 nm. The UV absorption of ClO

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and OCIO were monitored with an optical multichannel analyzer. The reaction was studied over a wide range of temperature, pressure, and initial reactant stoichiometry.

(a) Cl₂-sensitized continuous photolysis of Cl₂-O₃ mixtures in excess O₂. Decay of O₃ and formation of OCIO monitored by UV absorption.

Preferred Values

$$k_1 = 4.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 8.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_3 = 3.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_1 = 1.0 \times 10^{-12} \exp(-1590/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 260\text{--}390 \text{ K.}$$

$$k_2 = 3.0 \times 10^{-11} \exp(-2450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 260\text{--}390 \text{ K.}$$

$$k_3 = 3.5 \times 10^{-13} \exp(-1370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 260\text{--}390 \text{ K.}$$

Reliability

$$\Delta \log k_1 = \Delta \log k_2 = \Delta \log k_3 = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta (E_1/R) = \Delta (E_3/R) = \pm 300 \text{ K.}$$

$$\Delta (E_2/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The ClO+ClO reaction exhibits both bimolecular and termolecular reaction channels. The termolecular reaction, which leads to the formation of the ClOOCi dimer,

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dominates at high pressure (>0.013 bar at 298 K), but is not kinetically important at temperatures above ~283 K because of the instability of the dimer with respect to the reverse decomposition.

The recommended values for the individual reaction channels are those from the study of Nickolaisen et al. (1994). This study, using a flash photolysis-long pathlength UV absorption technique, is the most comprehensive study of this system, covering a wide range of temperature, initial reactant stoichiometry and pressure. These results (Nickolaisen et al., 1994) are preferred over the results of earlier studies of the total bimolecular rate coefficient at low pressures by Clyne and co-workers (1975) as discussed in the reviews of Watson (1977, 1980), and those of other studies reported by Cox and Derwent (1979), Hayman et al. (1986), Simon et al. (1990) and Horowitz et al. (1993).

The room temperature branching ratios from the study of Nickolaisen et al. (1994) are $k_1:k_2:k_3=0.29:0.50:0.21$. Horowitz et al. (1994) in their study of the temperature dependence of the channel branching ratios report slightly different values of $k_1:k_2:k_3=0.39:0.41:0.20$ at 298 K and observed distinctly non-Arrhenius behavior for k over the temperature range 285 K to 331 K. Their study (Horowitz et al., 1994) was carried out in excess O_2 , where the quantum yield for O_3 -photosensitized decomposition (which reflects Cl atom generation in this reaction) was consistently lower than in excess N_2 . The mechanistic explanation for this observation and for the apparent non-Arrhenius behavior remains obscure. The bath gas effect on $\Phi(-O_3)$ can be accounted for by the observed difference in the branching ratios in the presence of O_2 and N_2 , suggesting that O_2 is not involved in the $ClO+ClO$ reaction simply as a third-body quencher.

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III.A2.50



$$\Delta H^\circ = -75.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.0 \times 10^{-32} [\text{O}_2]$	298	Johnston et al., 1969	MM (a)
$2.0 \times 10^{-32} [\text{Ar}]$	298	Walker, 1972	DF-UVA (b)
$1.1 \times 10^{-32} [\text{O}_2]$	300	Basco and Hunt, 1979	FP-UVA (c)
$3.0 \times 10^{-32} [\text{N}_2]$	298	Cox et al., 1979	MM (d)
$6.0 \times 10^{-32} (T/300)^{-2.1} [\text{O}_2]$	268–338	Hayman et al., 1986	MM (e)
$(1.8 \pm 0.5) \times 10^{-32} (T/300)^{-3.6} [\text{N}_2]$	194–247	Sander et al., 1989	FP-UVA (f)
$(1.64 \pm 0.9) \times 10^{-32} (T/300)^{-4.4} [\text{N}_2]$	200–263	Trolier et al., 1990	FP-UVA (g)
$(1.32 \pm 0.08) \times 10^{-32} (T/300)^{-4.4} [\text{O}_2]$	200–263		
$1.22 \times 10^{-33} \exp[(833 \pm 34)/T] [\text{N}_2]$	195–390	Nickolaisen et al., 1994	FP-UVA (h)
$(1.96 \pm 0.24) \times 10^{-32} [\text{N}_2]$	300		
$(1.24 \pm 0.09) \times 10^{-32} [\text{O}_2]$	300		
$(2.5 \pm 0.4) \times 10^{-32} [\text{N}_2]$	300	Bloss, 1999	FP-UVA (i)
$1.7 \times 10^{-32} [\text{N}_2]$	300	Stark, 1999	PLP-UVA (j)
$1.1 \times 10^{-31} [\text{N}_2]$	200		
$(1.56 \pm 0.60) \times 10^{-32} (T/300)^{-4.5} [\text{N}_2]$	183–245	Bloss et al., 2001	FP-UVA (k)

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- (a) Photolysis of $\text{Cl}_2\text{-O}_2$ mixtures in the pressure range 0.07–1 bar.
- (b) Pressure range 1.3–10 mbar.
- (c) Pressure range 70–930 mbar.
- 5 (d) Photolysis of $\text{Cl}_2\text{-O}_2$ mixtures at 50–400 mbar.
- (e) Measurements in $\text{Cl}_2\text{-O}_2$ mixtures in the ratio 2:3, pressure range 7–30 mbar.
- (f) ClO radicals generated from $\text{Cl}_2\text{-Cl}_2\text{O}$ or $\text{Cl}_2\text{-O}_3$ mixtures with concentrations of bath gases N_2 , Ar or O_2 in the range of 10^{18} molecule cm^{-3} to 3×10^{-19} molecule cm^{-3} . Falloff extrapolations to k_0 and k_∞ used a value of $F_c=0.6$.
- 10 (g) ClO radicals generated from $\text{Cl}_2\text{-O}_3$ mixtures in the presence of 33 mbar to 800 mbar of He, N_2 , O_2 or SF_6 , ClO radicals and Cl_2O_2 monitored by long-path UV absorption. Falloff curves extrapolated with $F_c=0.6$.
- 15 (h) Pulsed laser photolysis of Cl_2 at $\lambda > 300$ nm in the presence of Cl_2O . ClO radicals generated by the reaction $\text{Cl} + \text{Cl}_2\text{O} \rightarrow \text{ClO} + \text{Cl}_2$ and monitored by UV absorption spectroscopy using either a photomultiplier for detection at 275.5 nm or an optical multichannel analyzer for detection over the wavelength range 270 nm to 280 nm. Measurements at 20–600 mbar. From a third-law analysis, a value of $\Delta H^\circ = -(75.7 \pm 0.9)$ kJ mol^{-1} was derived. Third-body efficiencies for the bath gases He, Ar, CF_4 , SF_6 and Cl_2 were also determined.
- 20 (i) ClO radicals generated by flash photolysis of $\text{Cl}_2\text{-Cl}_2\text{O-N}_2$ mixtures and detected by UV absorption. The bath gas pressure was varied between 0.25 bar and 1 bar. Falloff extrapolation used $F_c=0.6$. Small discrepancies between the various studies were attributed to the slightly different absorption cross-sections used.

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(j) ClO radicals generated by pulsed laser photolysis of Cl₂O between 0.1 bar and 1000 bar pressure of He and N₂. The observed pressure dependences differ from conventional falloff expressions, suggesting overlapping contributions from the energy transfer and radical-complex mechanism, as well as diffusion control at the highest pressures. The cited rate coefficients correspond to a representation of the falloff curve at pressures below 1 bar using $F_c=0.6$.

(k) See comment (i). Pressure range 30–930 mbar. Falloff extrapolation with $F_c=0.6$ and $k_\infty=(1.36\pm 0.2)\times 10^{-12} (T/300)^{-3.09} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

$k_0 = 2.0 \times 10^{-32} (T/300)^{-4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 190–390 K.

Reliability

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

$\Delta n = \pm 1.5$.

Comments on Preferred Values

The preferred values are based on the studies of Trolier et al. (1999) and Bloss et al. (2001) accounting for some falloff, see comments on high-pressure rate coefficients.

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High-pressure rate coefficients

Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6 \pm 2) \times 10^{-12}$	194–247	Sander et al., 1989	FP-UVA (a)
$(4.8 \pm 1.3) \times 10^{-12}$	200–263	Trolier et al., 1990	FP-UVA (b)
$(6 \pm 2) \times 10^{-12}$	195–390	Nickolaisen et al., 1994	FP-UVA (c)
$(5 \pm 3) \times 10^{-12}$	300	Bloss, 1999	FP-UVA (d)
4.5×10^{-12}	300	Stark, 1999	PLP-UVA (e)
7×10^{-12}	200		
$(1.36 \pm 0.22) \times 10^{-12} (T/300)^{-3.09}$	183–245	Bloss et al., 2001	FP-UVA (f)

Comments

- 5 (a) See comment (a) for k_0 .
- (b) See comment (g) for k_0 .
- (c) See comment (h) for k_0 . The k_{∞} value was obtained from falloff data measured below 250 K.
- (d) See comment (i) for k_0 .
- 10 (e) See comment (j) for k_0 . The cited rate coefficients are given for the energy-transfer mechanism only, such that the falloff curves below 1 bar are fitted. Above 1 bar pressure additional contributions from the radical-complex mechanism become increasingly important such that maximum values of k of

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$4.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K and $8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 200 K are reached near 200 bar, before they decrease because of diffusional control.

(f) See comment (i) and (k) for k_0 .

Preferred Values

5 $k_\infty = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 190–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 190 K to 300 K.

Comments on Preferred Values

10 It is difficult to provide a reasonable representation of k_0 , k_∞ and F_c , because there is ample evidence that this reaction is governed by a superposition of the energy transfer and the radical-complex mechanism. The pressure dependence at $P > 1$ bar looks anomalous (Stark, 1999). Likewise, the absolute value and the temperature coefficient of k_0 appear unusual. Neglecting these aspects, one may use the representation given
15 by Bloss et al. (2001) with $F_c = 0.6$ and k_0 and k_∞ as given in the table. We here choose a different representation with $F_c = 0.45$ and the preferred values given above which represent the data equally well at $P < 1$ bar. However, we keep in mind that the mechanistic complications of this system ask for different treatments. Difficulties in the theoretical analysis of the rate coefficients were also encountered by Bloss et al. (2001), Golden
20 (2003) and Zhu and Lin (2003).

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$$\Delta H^\circ = 75.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$9.81 \times 10^{-7} \exp[-(7980 \pm 320)/T] [\text{N}_2]$	260–310	Nickolaisen et al., 1994	FP-UVA (a)
$2.30 \times 10^{-18} [\text{N}_2]$	298		

Comments

10 (a) Photolysis of Cl_2 at $\lambda > 300 \text{ nm}$ in the presence of Cl_2O . ClO radicals were monitored with an optical multichannel analyzer at 270 nm to 280 nm. The pressure range used was 33 mbar to 400 mbar. Dissociation rate coefficients and equilibrium constants determined from analysis of two stages of ClO decay. From a third-law analysis, a value of $\Delta H^\circ = (75.7 \pm 0.9) \text{ kJ mol}^{-1}$ was derived. A value of the equilibrium constant $K_c = (1.24 \pm 0.18) \times 10^{-27} \exp\{8820/T\} \text{ cm}^3 \text{ molecule}^{-1}$ was obtained in good agreement with a determination by Cox and Hayman (1988).

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Preferred Values

$$k_0 = 2.3 \times 10^{-18} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 3.7 \times 10^{-7} \exp(-7690/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 260\text{--}310 \text{ K.}$$

Reliability

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

$$\Delta E/R = \pm 900 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the preferred values for the reverse reaction and the equilibrium constant from Nickolaisen et al. (1994) which agrees very well with the results of Cox and Hayman (1988).

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.8 \times 10^{15} \exp(-8820/T)$	260–310	Nickolaisen et al., 1994	FP-UVA (a)
6.7×10^2	298		

Comments

(a) See comment (a) for k_0 . Falloff curve constructed with $F_c=0.6$.

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Preferred Values

$$k_{\infty} = 1.1 \times 10^3 \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_{\infty} = 1.8 \times 10^{14} \exp(-7690/T) \text{ s}^{-1} \text{ over the temperature range } 260\text{--}310 \text{ K.}$$

Reliability

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

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

Comments on Preferred Values

The preferred values are based on the preferred values for the reverse reaction and the equilibrium constant from Nikolaisen et al. (1994). Falloff curves are constructed with $F_c=0.45$ like for the reverse reaction. One should keep in mind, however, that only data at $P < 1$ bar are represented. There is ample evidence that the reaction is governed by a superposition of the energy transfer and the radical-complex mechanism such that the chosen simple representation of the falloff curve does not apply rigorously.

References

- 15 Cox, R. A. and Hayman, G. D.: Nature, 332, 796, 1988.
Nicolaisen, S. L., Friedl, R. R., and Sander, S. P.: J. Phys. Chem., 98, 155, 1994.

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III.A2.52



$$\Delta H^\circ = -43.2 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.8 \times 10^{-31} [\text{N}_2]$	226	Parr et al., 1990	MM-UVA (a)
$(6.2 \pm 1.0) \times 10^{-32} (T/300)^{-4.7} [\text{N}_2]$	200–260	Burkholder et al., 1993	PLP-UVA (b)

Comments

10 (a) Experiments carried out with $\text{Cl}_2\text{-OCIO-N}_2$ mixtures in the pressure range 6.4–39 mbar. ClO monitored at 277.2 nm. The reaction was apparently close to the low pressure limit.

15 (b) Pulsed laser photolysis of mixtures of $\text{N}_2\text{O-Cl}_2\text{-OCIO-He}$ or $\text{CF}_2\text{Cl}_2\text{-OCIO-N}_2$ at 193 nm. From the first mixture, rate data were obtained while from the second mixture equilibrium constants and the absorption spectra of Cl_2O_3 between 220 nm and 320 nm were derived. From a second-law analysis of the data, together with those of Hayman and Cox (1989), $\Delta H^\circ = -(46.4 \pm 5.1) \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -(88.7 \pm 18.9) \text{ J mol}^{-1} \text{ K}^{-1}$ were derived. The kinetic data were obtained from a fit of the falloff curves between 33 mbar and 333 mbar total pressure using $F_c = 0.6$.

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Preferred Values

$k_0 = 6.2 \times 10^{-32} (T/300)^{-4.7} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

- 5 $\Delta \log k_0 = \pm 0.3$ at 298 K.
 $\Delta (n) = \pm 1$.

Comments on Preferred Values

10 The values of the extensive study of Burkholder et al. (1993) are adopted here. At 226 K the rate coefficient of Parr et al. (1990) is in reasonable agreement with our preferred value (and therefore with the data of Burkholder et al., 1993). Ab-initio calculations from Clark and Francisco (1997) predict the more stable structure of Cl_2O_3 to be ClOCl(O)O and result in a value of the enthalpy of the recombination reaction of $-45.6 \text{ kJ mol}^{-1}$.

High-pressure rate coefficients

15 Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.4 \pm 1.2) \times 10^{-11}$	200–260	Burkholder et al., 1993	(a)

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Comments

(a) See comment (b) for k_0 .

Preferred Values

$k_\infty = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

5 *Reliability*

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

Comments on Preferred Values

The preferred values are from Burkholder et al. (1993). The falloff extrapolation was done with $F_c=0.6$.

10 **References**

Burkholder, J. B., Mauldin III, R. L., Yokelson, R. J., Solomon, S., and Ravishankara, A. R.: J. Phys. Chem., 97, 7597, 1993.

Clark, J. and Francisco, J. S.: J. Phys. Chem. A, 101, 7145, 1997.

Hayman, G. D. and Cox, R. A.: Chem. Phys. Lett., 155, 1, 1989.

15 Parr, A. D., Wayne, R. P., Hayman, G. D., Jenkin, M. E., and Cox, R. A.: Geophys. Res. Lett., 17, 2357, 1990.

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III.A2.53



$$\Delta H^\circ = 43.2 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

No direct measurements are available.

Preferred Values

$$k_0 = 1.4 \times 10^{-10} \exp(-3810/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range 200–300 K.}$$

Reliability

$$10 \Delta \log k_0 = \pm 0.5 \text{ at 240 K.}$$

$$\Delta E/R = \pm 500 \text{ K.}$$

Comments on Preferred Values

15 The preferred values are from the preferred values for the reverse reaction $k_0 = 6.2 \times 10^{-32} (T/300)^{-4.7} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which were based on the measurements by Parr et al. (1990) and Burkholder et al. (1993), and the equilibrium constant $K_c = 9.7 \times 10^{-24} \exp(4940/T) \text{ cm}^3 \text{ molecule}^{-1}$ from Burkholder et al. (1993) and Hayman and Cox (1989).

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High-pressure rate coefficients

Rate coefficient data

No direct measurements are available.

Preferred Values

5 $k_{\infty} = 2.5 \times 10^{12} \exp(-4940/T) [\text{N}_2] \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$$\Delta \log k_{\infty} = \pm 0.5 \text{ at } 240 \text{ K.}$$

$$\Delta E/R = \pm 500 \text{ K.}$$

Comments on Preferred Values

10 See comments on Preferred Values for k_0 . Based on k_{∞} for the reverse reaction of $k_{\infty} = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Falloff curves constructed with $F_c = 0.6$.

References

Burkholder, J. B., Mauldin III, R. L., Yokelson, R. J., Solomon, S., and Ravishankara, A. R.: J. Phys. Chem., 97, 7597, 1993.

15 Hayman, G. D. and Cox, R. A.: Chem. Phys. Lett., 155, 1, 1989.

Parr, A. D., Wayne, R. P., Hayman, G. D., Jenkin, M. E., and Cox, R. A.: Geophys. Res. Lett., 17, 2357, 1990.

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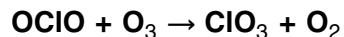
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III.A2.54



$$\Delta H^\circ = -20 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.20 \pm 0.15) \times 10^{-19}$	298	Birks et al., 1977	(a)
$2.3 \times 10^{-12} \exp[-(4730 \pm 630)/T]$	262–298	Wongdontri-Stuper et al., 1979	PLP-UVA (b)
3.0×10^{-19}	298		

Comments

(a) Static system, rate coefficient determined by monitoring the loss of O_3 in excess OCIO and also loss of OCIO in excess O_3 . Both species were measured by UVA; O_3 at 254 nm and OCIO at 366 nm.

(b) The decay of OCIO in excess O_3 was monitored by UVA at 400 nm. The reaction rate was also determined by the pulsed photolysis of $\text{Cl}_2\text{-O}_2$ mixtures at 366 nm to produce OCIO, followed by monitoring OCIO decay.

Preferred Values

$k = 3.0 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.1 \times 10^{-12} \exp(-4700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–2462

300 K.

Reliability

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

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

5 *Comments on Preferred Values*

The preferred values are based on the results reported in the study of Wongdontri-Stuper et al. (1979). Within the indicated uncertainty limits, the preferred values encompass the lower room temperature value reported by Birks et al. (1977).

References

- 10 Birks, J. W., Shoemaker, B., Leck, T. J., Borders, R. A., and Hart, L. J.: J. Chem. Phys., 66, 4591, 1977.
- Wongdontri-Stuper, W., Jayanty, R. K. M., Simonaitis, R., and Heicklen, J.: J. Photochem., 10, 163, 1979.

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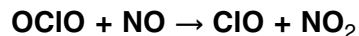
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$$\Delta H^\circ = -50.0 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.4 \pm 0.5) \times 10^{-13}$	298	Bemand et al., 1973	DF-MS
$1.04 \times 10^{-13} \exp[(347 \pm 58)/T]$	220–367	Li et al., 2002	DF-MS
$(3.55 \pm 0.30) \times 10^{-13}$	298		

Preferred Values

$k = 3.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.1 \times 10^{-13} \exp(350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–370 K.

Reliability

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

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

Comments on Preferred Values

The two available studies of this reaction (Bemand et al., 1973; Li et al., 2002), both using the same method, show good agreement at the common temperature, 298 K, and the recommendation at this temperature is the average result. The recommended

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temperature dependence is provided by the study of Li et al. (2002), with a slight correction to the pre-exponential factor to match the preferred value at 298 K.

References

Bemand, P. P., Clyne, M. A. A., and Watson, R. T.: J. Chem. Soc. Faraday Trans., 1, 69, 1356, 1973.

Li, Z., Wuebbles, D., and Pylawka, N. J.: Chem. Lett., 354, 491, 2002.

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OCIO + NO₃ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$< 1 \times 10^{-15}$	300	Biggs et al., 1991	DF-UV
2×10^{-14}	298	Fiedl et al., 1992	(a)
2×10^{-14}	220		
$< 6 \times 10^{-17}$	298–300	Boyd et al., 1996	(b)

5 **Comments**

(a) The experiments were carried out in a long-path absorption flow reactor. NO₃ radicals were generated by the reaction of F atoms with HNO₃ or of Cl atoms with ClONO₂. The products were analysed by IR and UV absorption measurements. Rate constant at 298 K derived by computer simulation of NO₃, OCIO and ClO profiles, and assuming NO₂+O₂+ClO are products. At 220 K and 5.3 mbar He, formation of chlorylnitrate (O₂ClONO₂) in a termolecular reaction channel was observed, with an apparent rate constant of $2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. At this temperature the rate constant for the bimolecular channel was derived to be $2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

15 (b) Room temperature studies at low pressure in discharge stopped flow (typically 10.7 mbar), slow flow (typically 8 mbar) and discharge flow (2.7 mbar) experiments. Detection of both NO₃ and OCIO was achieved using absorption

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spectroscopy. The slow flow experiments are comparable to those of Friedl et al. (1992).

Preferred Values

No recommendation is given.

5 *Comments on Preferred Values*

The available results of the studies of this reaction are very divergent. In their later study, Boyd et al. (1996) were unable to interpret their observations, obtained in three different set ups, in terms of a gas-phase reaction between NO_3 and OCIO, and suggest that heterogeneous processes play an important role in their study, and potentially therefore also in the similar study of Friedl et al. (1992). Further work is clearly needed to resolve these discrepancies, and until this is available no recommendation is given, other than to note that the reaction is slow.

References

Biggs, P., Harwood, M. H., Parr, A. D., and Wayne, R. P.: J. Phys. Chem., 95, 7746, 1991.

Boyd, A. A., Marston, G., and Wayne, R. P.: J. Phys. Chem., 100, 130, 1996.

Friedl, R. R., Sander, S. P., and Yung, Y. L.: J. Phys. Chem., 96, 7490, 1992.

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III.A2.57



$$\Delta H^\circ = -71.2 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

5

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$< 1 \times 10^{-19}$	195–217	DeMore and Tschuikow-Roux, 1990	(a)

Comments

(a) Photolysis ($\lambda > 300 \text{ nm}$) of $\text{Cl}_2\text{-O}_3$ or $\text{Cl}_2\text{-Cl}_2\text{O}$ mixtures, both in the gas phase and in the cryogenic solvents CF_4 , CO_2 and N_2O . The quantum yield of O_3 loss was measured.

10

Preferred Values

$k < 1 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 200 K.

Comments on Preferred Values

The recommended upper limit to the rate coefficient is that determined by DeMore and Tschuikow-Roux (1990) from measurements of the quantum yield of O_3 loss in the photolysis of $\text{Cl}_2\text{-O}_3$ mixtures at $\lambda > 300 \text{ nm}$. The experiments were very sensitive

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to this reaction. Reaction at a rate greater than this upper limit would have had a marked effect on the quantum yield of ozone loss and also would have resulted in a dependence of the quantum yield on the ozone concentration; however, neither effect was observed (DeMore and Tschuikow-Roux, 1990). These measurements refer to a temperature of about 200 K; the value of this rate coefficient at higher temperatures would be of no atmospheric significance because of the thermal decomposition of the Cl_2O_2 dimer.

References

DeMore, W. B. and Tschuikow-Roux, E.: J. Phys. Chem., 94, 5856, 1990.

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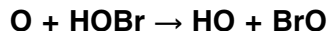
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Appendix 3: BrO_x Reactions

III.A3.58



$$\Delta H^\circ \leq -36 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.5 \pm 0.4) \times 10^{-11}$	298	Monks et al., 1993	DL-MS
$1.4 \times 10^{-10} \exp[-(430 \pm 260)/T]$	233–423	Nesbit et al., 1995	DF-MS
$(2.5 \pm 0.6) \times 10^{-11}$	298		
$(3.1 \pm 0.2) \times 10^{-11}$	300	Kukui et al., 1996	DF-MS

Preferred Values

$$k = 2.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.2 \times 10^{-10} \exp(-430/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 230\text{--}430 \text{ K.}$$

Reliability

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

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

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Comments on Preferred Values

The preferred rate coefficient at 298 K is the mean of the values of Nesbitt et al. (1995) and Kukui et al. (1996) and the temperature dependence is that of Nesbitt et al. (1995) with the *A*-factor adjusted to yield the preferred rate coefficient at 298 K.

- 5 Note that the rate coefficient for this reaction is almost a factor of 200 greater than that for the corresponding reaction of O(³P) atoms with HOCl (IUPAC, 2005).

References

IUPAC: <http://www.iupac-kinetic.ch-cam.ac.uk/>, 2005.

Kukui, A., Kirchner, U., Benter, T., and Schindler, R. N.: Ber. Bunsenges. Phys. Chem., 100, 455, 1996.

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Monks, P. S., Nesbitt, F. L., Scanlon, M., and Stief, L. J.: J. Phys. Chem., 97, 11 699, 1993.

Nesbitt, F. L., Monks, P. S., Payne, W. A., Stief, L. J., and Toumi, R.: Geophys. Res. Lett., 22, 827, 1995.

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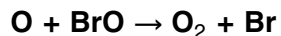
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III.A3.59



$$\Delta H^\circ = -257 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.5^{+2.5}_{-1.5}) \times 10^{-11}$	298	Clyne et al., 1976	DF-RF (a)
$1.9 \times 10^{-11} \exp[(230 \pm 150)/T]$	231–328	Thorn et al., 1995	PLP-A/RF (b)
$(4.1 \pm 0.6) \times 10^{-11}$	298		

Comments

- (a) Measurements of O atom consumption rates and Br atom production rates in the O+Br₂ reaction were interpreted to give an estimate of $k(\text{O}+\text{BrO} \rightarrow \text{O}_2+\text{Br})$.
- (b) Pulsed laser flash photolysis system with detection of BrO radicals by long path absorption and of O(³P) atoms by resonance fluorescence.

Preferred Values

$k = 4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.9 \times 10^{-11} \exp(230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–330 K.

Reliability

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

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

Comments on Preferred Values

- 5 The preferred value is based on the direct study of Thorn et al. (1995) in which the decay of $O(^3P)$ in the presence of excess BrO was monitored. Clyne et al. (1976) derived an indirect estimate of the room temperature value which was approximately 40% lower than the preferred value given above.

References

- 10 Clyne, M. A. A., Monkhouse, P. B., and Townsend, L. W.: *Int. J. Chem. Kinet.*, 8, 425, 1976.
- Thorn, R. P., Cronkhite, J. M., Nicovich, J. M., and Wine, P. H.: *J. Chem. Phys.*, 102, 4131, 1995.

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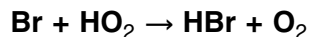
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III.A3.60



$$\Delta H^\circ = -162.8 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.4 \times 10^{-11} \exp[-(590 \pm 140)/T]$	260–390	Toohey et al., 1987	DF-LMR/RF (a)
$(2.0 \pm 0.3) \times 10^{-12}$	298		
$(1.5 \pm 0.2) \times 10^{-12}$	298	Laverdet et al., 1990	DF-EPR (b)
$4.9 \times 10^{-12} \exp[-(310 \pm 40)/T]$	230–355	Bedjanian et al., 2001	DF-MS (c)
$(1.71 \pm 0.20) \times 10^{-12}$	297		

Comments

(a) Br atoms generated either directly by discharge of Br_2 , or from the addition of diluted Br_2 to an excess of $\text{O}(^3\text{P})$ atoms. HO_2 radicals were generated by the $\text{F} + \text{H}_2\text{O}_2$ reaction. HO_2 radicals and Br atoms were monitored by laser magnetic resonance and resonance fluorescence, respectively. k was determined from pseudo-first order decay of HO_2 in the presence of excess Br.

(b) Br atoms generated either directly by discharge of Br_2 , or from the $\text{Cl} + \text{CH}_2 = \text{CHBr}$ reaction. HO_2 radicals were generated from the reaction of Cl with CH_3OH in the presence of O_2 . k was determined from pseudo-first order decay of HO_2 in the presence of excess Br. A reinterpretation of previous indirect measurements

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conducted in the same laboratory (Poulet et al., 1984) is also given. This yielded revised values of k in the range $(1.0\text{--}2.2)\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$.

(c) Br atoms generated either directly by discharge of Br_2 , or from the $\text{H}+\text{Br}_2$ or $\text{Cl}+\text{Br}_2$ reactions. HO_2 radicals were generated by the $\text{F}+\text{H}_2\text{O}_2$ reaction. k was determined from pseudo-first order decay of HO_2 in the presence of excess Br.

Preferred Values

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

$k = 7.7 \times 10^{-12}\text{ exp}(-450/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the temperature range 230–390 K.

Reliability

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

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

Comments on Preferred Values

The preferred value at 298 K is the mean of the results of Toohey et al. (1987), Laverdet et al. (1990) and Bedjanian et al. (2001), which are all in acceptable agreement. The preferred Arrhenius expression is based on the mean of the E/R values from the temperature dependence studies of Toohey et al. (1987) and Bedjanian et al. (2001) combined with a pre-exponential factor adjusted to give the preferred value of k at 298 K. The uncertainty in the preferred value of E/R reflects the fact that the values reported by Toohey et al. (1987) and Bedjanian et al. (2001) differ by almost a factor of two. The observed kinetics are consistent with the mechanism proceeding via direct hydrogen atom abstraction to yield HBr, as also indicated by theoretical studies of the reaction (Sumathi and Peyerimhoff, 1999).

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Bedjanian, Y., Riffault, V., Le Bras, G., and Poulet, G.: J. Phys. Chem. A, 105, 573, 2001.

5 Laverdet, G., Le Bras, G., Mellouki, A., and Poulet, G.: Chem. Phys. Lett., 172, 430, 1990.

Poulet, G., Laverdet, G., and Le Bras, G.: J. Chem. Phys., 80, 1922, 1984.

Sumathi, R. and Peyerimhoff, S. D.: Phys. Chem. Chem. Phys., 1, 3973, 1999.

Toohey, D. W., Brune, W. H., and Anderson, J. G.: J. Phys. Chem., 91, 1215, 1987.

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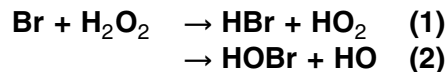
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III.A3.61



$$\Delta H^\circ(1) = 2.8 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) \leq 6 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$< 1.5 \times 10^{-15}$	298	Leu, 1980	DF-MS
$< 3.0 \times 10^{-15}$	417		
$< 2.0 \times 10^{-15}$	~ 298	Posy et al., 1981	DF-MS
$< 5 \times 10^{-16}$	298	Toohey et al., 1987	DF-RF (a)
$< 5 \times 10^{-16}$	378		

Comments

(a) Decays of Br radicals were monitored in the presence of excess H_2O_2 . Measurement of HO_2 and HO radical products by LMR allowed upper limits of $5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to be derived for both channel (1) and channel (2).

Preferred Values

$k < 5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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Comments on Preferred Values

The upper limit to the preferred value is based on the data of Toohey et al. (1987) who also obtained the same upper limit at 378 K. The upper limits to the rate constant of Toohey et al. (1987) are consistent with the previous higher upper limits of Leu (1980) and Posey et al. (1981).

References

Leu, M.-T.: Chem. Phys. Lett., 69, 37, 1980.

Posey, J., Sherwell, J., and Kaufman, M.: Chem. Phys. Lett., 77, 476, 1981.

Toohey, D. W., Brune, W. H., and Anderson, J. G.: J. Phys. Chem., 91, 1215, 1987.

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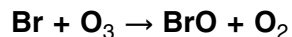
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$$\Delta H^\circ = -135 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.2 \pm 0.2) \times 10^{-12}$	298	Clyne and Watson, 1975	DF-MS
$3.34 \times 10^{-11} \exp[-(978 \pm 36)/T]$	224–422	Leu and DeMore, 1977	DF-MS
$(1.16 \pm 0.16) \times 10^{-12}$	298		
$7.74 \times 10^{-12} \exp[-(603 \pm 16)/T]$	200–360	Michael et al., 1978	FP-RF
$(1.01 \pm 0.18) \times 10^{-12}$	298		
$9.45 \times 10^{-12} \exp[-(659 \pm 64)/T]$	234–360	Michael and Payne, 1979	DF-RF
$(1.12 \pm 0.07) \times 10^{-12}$	298		
$3.28 \times 10^{-11} \exp[-(944 \pm 30)/T]$	248–418	Toohey et al., 1988	DF-RF
$1.42 \pm 0.03) \times 10^{-12}$	298		
$1.50 \times 10^{-11} \exp[-(775 \pm 30)/T]$	195–392	Nicovich et al., 1990	PLP-RF
$(1.11 \pm 0.07) \times 10^{-12}$	298		
$(1.2 \pm 0.1) \times 10^{-12}$	298	Ninomiya et al., 2000	PLP-CRDS (a)

Comments

- (a) BrO formation was monitored by cavity ring down spectroscopy at 338.5 nm. The background signal was monitored at 338.1 nm.

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Preferred Values

$k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.7 \times 10^{-11} \exp(-800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 190–430 K.

5 *Reliability*

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

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

Comments on Preferred Values

10 The recommended Arrhenius expression is based on a fit to the results of Clyne and Watson (1975), Leu and DeMore (1977), Michael et al. (1978), Michael and Payne (1979), Toohey et al. (1988), Nicovich et al. (1990) and Ninomiya et al. (2000).

References

- Clyne, M. A. A. and Watson, R. T.: J. Chem. Soc. Faraday Trans., 1, 71, 336, 1975.
Leu, M. T. and DeMore, W. B.: Chem. Phys. Lett., 48, 317, 1977.
15 Michael, J. V., Lee, J. H., Payne, W. A., and Stief, L. J.: Chem. Phys., 68, 4093, 1978.
Michael, J. V. and Payne, W. A.: Int. J. Chem. Kinet., 11, 799, 1979.
Nicovich, J. M., Kreutter, K. D., and Wine, P. H.: Int. J. Chem. Kinet., 22, 399, 1990.
Ninomiya, Y., Hashimoto, S., Kawasaki, M., and Wallington, T. J.: Int. J. Chem. Kinet., 32, 125, 2000.
20 Toohey, D. W., Brune, W. H., and Anderson, J. G.: Int. J. Chem. Kinet., 20, 131, 1988.

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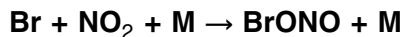
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$$\Delta H^\circ = -81 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.7 \pm 0.7) \times 10^{-31} [\text{He}]$	298	Mellouki et al., 1989	DF-EPR/MS (a)
$(2.75 \pm 0.55) \times 10^{-31} [\text{He}]$	298	Kreutter et al., 1991	PLP-RF (b)
$4.24 \times 10^{-31} (T/300)^{-2.4} [\text{N}_2]$	259–346		

Comments

(a) Pressure range 0.8–2.8 mbar.

(b) Pressure range 16.7–933 mbar; measurements in the bath gases He, Ar, H₂, N₂, CO₂, CF₄ and SF₆. Falloff curves were analyzed with $F_c=0.59$ at 259 K, 0.55 at 298 K, and 0.50 at 346 K.

Preferred Values

$k_0 = 4.2 \times 10^{-31} (T/300)^{-2.4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–350 K.

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Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Values

- 5 The preferred values are based on the results of the study of Kreutter et al. (1991). The falloff curves are represented with $F_c=0.55$. Broske and Zabel (1998) as well as Orlando and Burkholder (2000) identified BrONO to be the major product of the reaction and reevaluated the thermochemistry data from Kreutter et al. (1991).

High-pressure rate coefficients

10 Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
2.66×10^{-11}	259–346	Kreutter et al., 1991	PLP-RF (a)

Comments

(a) See comment (b) for k_0 .

Preferred Values

- 15 $k_\infty = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–350 K.

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Reliability

$\Delta \log k_{\infty} = \pm 0.4$ over the range 250–350 K.

Comments on Preferred Values

See comments on k_0 . There is only a single determination of k_{∞} , but the measured falloff curve appears well behaved with rate coefficients close to those of the reactions I+NO+M and I+NO₂+M.

References

Broske, R. and Zabel, F.: J. Phys. Chem. A, 102, 8626, 1998.

Kreutter, K. D., Nicovich, J. M., and Wine, P. H.: J. Phys. Chem., 95, 4020, 1991.

10 Mellouki, A., Laverdet, G., Jourdain, J. L., and Poulet, G.: Int. J. Chem. Kinet., 21, 1161, 1989.

Orlando, J. J. and Burkholder, J. B.: J. Phys. Chem. A, 104, 2048, 2000.

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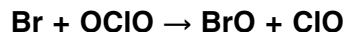
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$$\Delta H^\circ = 15 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
4.2×10^{-13}	298	Clyne and Watson, 1977	DF-MS (a)
$2.5 \times 10^{-11} \exp(-1336/T)$	267–423	Toohey, 1988	DF-RF (b)
$(2.82 \pm 0.03) \times 10^{-13}$	299		

Comments

(a) MS detection of OCIO in an excess of Br atoms. The observed decays were first-order, but computer modeling was used to correct for the effects of the reverse reaction.

(b) The measured rate coefficients ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ units) were: 267 K, $(1.70 \pm 0.03) \times 10^{-13}$; 294 K, $(2.63 \pm 0.04) \times 10^{-13}$; 299 K, $(2.82 \pm 0.03) \times 10^{-13}$; 325 K, $(4.03 \pm 0.07) \times 10^{-13}$; 351 K, $(5.45 \pm 0.22) \times 10^{-13}$; 385 K, $(7.88 \pm 0.24) \times 10^{-13}$; and 423 K, $(1.06 \pm 0.04) \times 10^{-12}$. A unit-weighted least-squares fit of these data to the Arrhenius expression results in $k = 2.5 \times 10^{-11} \exp(-1336/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 267–423 K.

Preferred Values

$k = 3.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.7 \times 10^{-11} \exp(-1300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–430 K.

5 *Reliability*

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

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

Comments on Preferred Values

10 The preferred value at 298 K is the mean of the values reported by Clyne and Watson (1977) and Toohey (1988). In the former study (Clyne and Watson, 1977) corrections were made for the effects of the reverse reaction, which was not done in the earlier study by Clyne and Coxon (1967) and which is therefore not used in this evaluation. The temperature dependence of k obtained by Toohey (1988) is accepted, but with substantial uncertainty limits in the absence of confirmatory studies, and is combined
15 with the preferred value of k at 298 K to obtain the preferred Arrhenius expression.

References

Clyne, M. A. A. and Coxon, J. A.: Proc. Roy. Soc. London A, 298, 424, 1967.

Clyne, M. A. A. and Watson, R. T.: J. Chem. Soc. Faraday Trans., 1, 73, 1169, 1977.

20 Toohey, D. W.: Kinetic and Mechanistic Studies of Reactions of Bromine and Chlorine Species Important in the Earth's Stratosphere, Ph.D. Thesis, Harvard University, Cambridge, MA, 1988.

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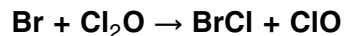
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$$\Delta H^\circ = -72.8 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

5

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.1 \times 10^{-11} \exp[-(520 \pm 260)/T]$ $(3.79 \pm 0.38) \times 10^{-12}$	220–298 298	Sander and Friedl, 1989	FP-AS (a)
$2.1 \times 10^{-11} \exp[-(435 \pm 30)/T]$ $(4.8 \pm 0.2) \times 10^{-12}$	233–402 298	Stevens and Anderson, 1992	DF-RF

Comments

(a) Flash photolysis ($\lambda > 300 \text{ nm}$) of Br_2 in the presence of an excess of Cl_2O at 130 mbar pressure of Ar. ClO radical concentrations were monitored by long-path UV absorption at 275.2 nm.

10

Preferred Values

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

$k = 2.1 \times 10^{-11} \exp(-470/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–410 K.

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Reliability

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

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

Comments on Preferred Values

5 The studies of Sander and Friedl (1989) and Stevens and Anderson (1992), which used totally different techniques, are in excellent agreement. The preferred values are based on the results of these two studies (Sander and Friedl, 1989; Stevens and Anderson, 1992). The significantly lower value (by a factor of 4) reported earlier by Basco and Dogra (1971) is not used in the evaluation. In the same study, Basco and
10 Dogra (1971) reported a value for $k(\text{Cl} + \text{Cl}_2\text{O})$ more than two orders of magnitude less than that recommended in the present evaluation, suggesting errors in their method of determining the ClO radical concentration which was used to monitor the progress of the reaction.

References

- 15 Basco, N. and Dogra, S. K.: Proc. Roy. Soc. London, A323, 401, 1971.
Sander, S. P. and Friedl, R. R.: J. Phys. Chem., 93, 4764, 1989.
Stevens, P. S. and Anderson, J. G.: J. Phys. Chem., 96, 1708, 1992.

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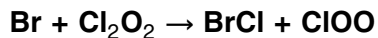
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$$\Delta H^\circ = -127.4 \text{ kJ}\cdot\text{mol}^{-1}$$

5 There are no published measurements of this rate coefficient.

Preferred Values

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

Reliability

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

10 *Comments on Preferred Values*

The preferred value is based on the results of an unpublished discharge flow study of R. R. Friedl (1991). Substantial uncertainties are suggested in the absence of confirmatory studies.

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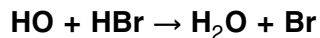
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$$\Delta H^\circ = -130.9 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.1 \pm 1.0) \times 10^{-12}$	295	Takacs and Glass, 1973	DF-EPR (a)
$(1.19 \pm 0.14) \times 10^{-11}$	249–416	Ravishankara et al., 1979	PLP-RF
$(6.01 \pm 0.32) \times 10^{-12}$	300	Husain et al., 1981	FP-RF
$(9.2 \pm 0.7) \times 10^{-12}$	~ 298	Jourdain et al., 1981	DF-EPR
$(1.12 \pm 0.045) \times 10^{-11}$	298 ± 4	Cannon et al., 1984	FP-LIF
$(1.1 \pm 0.1) \times 10^{-11}$	298	Ravishankara et al., 1985	PLP-RF/LIF
$(2.97 \pm 0.46) \times 10^{-11}$	170	Sims et al., 1994	PLP-LIF (b,c)
$(1.16 \pm 0.04) \times 10^{-11}$	295		
$(8 \pm 1) \times 10^{-12}$	173	Atkinson et al., 1997	FP-LIF (b,d)
$(1.5 \pm 0.4) \times 10^{-11}$	194		
$(1.0 \pm 0.3) \times 10^{-11}$	194		
$(1.3 \pm 0.2) \times 10^{-11}$	222		
$(1.1 \pm 0.1) \times 10^{-11}$	242		
$5.5 \times 10^{-12} \exp[(204 \pm 45)/T]$	230–360	Bedjanian et al., 1999	DF-MS (e)
$(1.11 \pm 0.12) \times 10^{-11}$	298		
$(1.72 \pm 0.40) \times 10^{-11}$	185	Jaramillo and Smith, 2001;	FP-LIF (b,d)
$(1.31 \pm 0.35) \times 10^{-11}$	224	Jaramillo et al., 2002	

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- (a) Rate coefficient obtained from a computer simulation of 4 reactions.
- (b) Expansion of gas through a Laval nozzle to provide a collimated flow of cold gas at a uniform temperature, density and velocity.
- 5 (c) Experiments were carried out over the temperature range 23–295 K, with the measured rate coefficient decreasing with increasing temperature from $(1.07 \pm 0.04) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 23 K to $(1.16 \pm 0.04) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K. Combined with the rate coefficients of Ravishankara et al. (1979) the temperature-dependent expression
- 10 $k = (1.26 \pm 0.24) \times 10^{-11} (T/298)^{-(0.86 \pm 0.10)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived.
- (d) Rate coefficients were measured over the temperature range 76–242 K, with the rate coefficient decreasing from $(3.0 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 92 K and $(2.9 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 76 K to $(1.1 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 242 K. Above 150 K the rate coefficient was independent of temperature, within the experimental uncertainties.
- 15 (e) The cited Arrhenius expression is obtained from a unit-weighted least-squares analysis of the measured rate coefficients. The cited uncertainty is one least-squares standard deviation.
- (f) Rate coefficients were obtained over the temperature range 120–224 K for HO+HBr, DO+HBr, HO+DBr and DO+DBr (Jaramillo and Smith, 2001), and over the temperature range 48–224 K for HO+HBr (Jaramillo et al., 2002). The measured rate coefficients decreased with increasing temperature (Jaramillo and Smith, 2001; Jaramillo et al., 2002). The available database (Takacs and Glass, 1973; Smith and Zellner, 1974; Ravishankara et al., 1979, 1985; Husain et al., 1981; Jourdain et al., 1981; Cannon et al., 1984; Sims et al., 1994; Atkinson et al., 1997; Bedjanian et al., 1999; Jaramillo and Smith, 2001; Jaramillo
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et al., 2002) (23–416 K) was fit (Jaramillo et al., 2002) about equally well by the expressions $k=1.11 \times 10^{-11} (T/298)^{-0.91} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ or $k=1.06 \times 10^{-11} (T/298)^{-1.09} \exp(-10.5/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

- 5 $k = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 5.5 \times 10^{-12} \exp(205/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 180–360 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta (E/R) = \pm 250 \text{ K}$.

10 *Comments on Preferred Values*

The studies of Sims et al. (1994), Atkinson et al. (1997), Jaramillo and Smith (2001) and Jaramillo et al. (2002), carried out using expansions through a Laval nozzle to achieve temperatures down to 23 K (Sims et al., 1994), show reaction rate coefficients which increase with decreasing temperature, as does the 230–360 K study of Bedjanian et al. (1999). The rate coefficients measured by Bedjanian et al. (1999) at 230 K and by Jaramillo and Smith (2001, 2002) at 224 K are in good agreement. The Jaramillo and Smith (2001, 2002) data are assumed to supersede the earlier data of Atkinson et al. (1997). The preferred values are obtained from a least-squares analysis of the rate coefficients of Ravishankara et al. (1985) and Bedjanian et al. (1999) and the 185 and 224 K rate coefficients of Jaramillo and Smith (2001, 2002). The preferred 298 K rate coefficient is in good agreement with the measured values of Ravishankara et al. (1979), Jourdain et al. (1981), Cannon et al. (1984) and Sims et al. (1994) and the recommended Arrhenius expression yields predicted rate coefficients which are

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in good agreement (within 15%) with those measured by Ravishankara et al. (1979) except at 416 K where the discrepancy is 35%.

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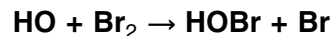
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$$\Delta H^\circ \geq -12 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

5

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.2 \pm 0.7) \times 10^{-11}$	298 ± 2	Poulet et al., 1983	DF-LIF/EPR
$(5.28 \pm 0.63) \times 10^{-11}$	298 ± 3	Loewenstein and Anderson, 1984	DF-RF
$(2.8 \pm 1.2) \times 10^{-11}$	262–303	Boodaghians et al., 1987	DF-RF (a)
$(3.4 \pm 1.2) \times 10^{-11}$	293		
$1.98 \times 10^{-11} \exp[(238 \pm 70)/T]$	235–357	Gilles et al., 1999	PLP-LIF
$(4.80 \pm 0.70) \times 10^{-11}$	298		
$1.8 \times 10^{-11} \exp[(235 \pm 50)/T]$	230–360	Bedjanian et al., 1999	DF-MS
3.96×10^{-11}	298		

Comments

- (a) A least-squares fit of the measured rate coefficients results in $k = 5.8 \times 10^{-10} \exp[-(866 \pm 1107)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, consistent with a temperature-independent rate coefficient over the small temperature range studied.

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Preferred Values

$k = 4.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.0 \times 10^{-11} \exp(240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–360 K.

Reliability

5 $\Delta \log k = \pm 0.10$ at 298 K.

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

Comments on Preferred Values

The rate coefficient is reasonably well determined at room temperature, and the recommended value is the mean of those reported by Poulet et al. (1983), Loewenstein and Anderson (1984), Gilles et al. (1999) and Bedjanian et al. (1999). The rate coefficients of Boodaghians et al. (1987) have large uncertainties and are consistent with a zero temperature dependence over the range 262–303 K. Gilles et al. (1999) and Bedjanian et al. (1999) measured a small negative temperature dependence over the significantly wider temperature range of 230–360 K. Accordingly, the temperature dependence of Gilles et al. (1999) and Bedjanian et al. (1999) is preferred, and the pre-exponential factor, A , is adjusted to fit the preferred 298 K rate coefficient. Poulet et al. (1983), Loewenstein and Anderson (1984) and Bedjanian et al. (1999) determined that the products are $\text{Br} + \text{HOBr}$, with the alternative reaction pathway leading to $\text{HBr} + \text{BrO}$ accounting for <1% of the overall reaction at 298 K (Loewenstein and Anderson, 1984).

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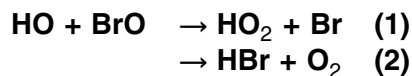
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III.A3.69



$$\Delta H^\circ(1) = -30 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -193 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(7.5 \pm 4.2) \times 10^{-11}$	300	Bogan et al., 1996	DF-MS (a)
$(4.5 \pm 1.8) \times 10^{-11}$	298 ± 3	Gilles et al., 2001	DF (b)
$1.65 \times 10^{-11} \exp[(250 \pm 50)/T]$	230–355	Bedjanian et al., 2001	DF-MS (c)
$(3.6 \pm 0.9) \times 10^{-11}$	300		(d)
$(3.9 \pm 1.0) \times 10^{-11}$	298		(e)
$(3.85 \pm 0.70) \times 10^{-11}$	299		(f)
<i>Branching ratios</i>			
$k_2/k \leq 0.03$	298	Bedjanian et al., 2001	DF-MS (g)

Comments

(a) BrO radicals generated by passing a $\text{O}_2\text{-Br}_2\text{-He}$ mixture through a microwave discharge. HO radicals generated by the reaction of F atoms (generated in a second microwave discharge) with H_2O . BrO radical concentrations were obtained by

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titration with NO and measurement of the resulting NO₂ by MS. HO radical concentrations were obtained by titration with Br₂ and measurement of the depletion of Br₂ by MS. The rate coefficient was derived from modelling using a chemical mechanism involving 18 reactions.

5 (b) BrO radicals generated from Br+O₃ reaction (following discharge of Br₂). HO radicals generated from pulsed 248 nm laser photolysis of O₃ in the presence of H₂O. BrO and HO were measured by UV absorption and LIF, respectively. Experiments carried out under pseudo-first order conditions with HO in excess.

10 (c) BrO generated from either from O(³P)+Br₂ (following discharge of O₂), or from Br+O₃ (following discharge of Br₂). Br was also generated by F+HBr (following discharge of F₂) for mechanistic studies. HO was generated from either H+NO₂ (following discharge of H₂ or F+H₂), or F+H₂O (following discharge of F₂). BrO and HO concentrations were measured directly at their parent peaks. Experiments carried out under pseudo-first order conditions with HO in excess. *k* also determined relative to *k*(HO+Br₂) in a separate series of experiments. Results of the two methods are in good agreement and the reported rate coefficient is based on the combined dataset.

(d) HO generated by H+NO₂.

(e) HO generated by F+H₂O.

20 (f) Relative rate measurement.

(g) Based on detection of HBr.

Preferred Values

$k = 4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.8 \times 10^{-11} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–350 K.

Reliability

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

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

Comments on Preferred Values

5 The preferred value at 298 K is based on the room temperature data of Gilles et al. (2001) and Bedjanian et al. (2001). The previous study of Bogan et al. (1996) is also consistent with this recommendation. The preferred Arrhenius expression is based on the E/R value from the temperature dependence study of Bedjanian et al. (2001) combined with a pre-exponential factor adjusted to give the preferred value of k at
10 298 K. The results of Bedjanian et al. (2001) are consistent with channel (a) being the dominant, if not sole, pathway. This conclusion is supported by the theoretical study of Sumathi and Peyerimhoff (1999).

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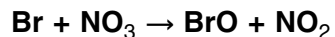
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III.A3.70



$$\Delta H^\circ = -33 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.6 \pm 0.7) \times 10^{-11}$	298	Mellouki et al., 1989	DF-EPR (a)

Comments

(a) The decays of Br atoms in excess concentrations of the NO_3 radical were monitored by EPR. Computer simulations of the decays were carried out with a mechanism consisting of five reactions.

Preferred Values

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

Reliability

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

Comments on Preferred Values

The preferred value is based on the sole study of Mellouki et al. (1989).

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Mellouki, A., Poulet, G., Le Bras, G., Singer, R., Burrows, J. P., and Moortgat, G. K.: J. Phys. Chem., 93, 8017, 1989.

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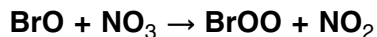
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III.A3.71



$$\Delta H^\circ = -52 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(0.3\text{--}3.0) \times 10^{-12}$	298	Mellouki et al., 1989	DF-EPR (a)

Comments

(a) The decays of Br atoms and BrO radicals were monitored by EPR. Computer simulations of the results were carried out with a mechanism consisting of five reactions.

Preferred Values

$$k = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

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

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Comments on Preferred Values

The preferred value is based on the room temperature results of Mellouki et al. (1989). This study (Mellouki et al., 1989), using the discharge flow-EPR technique, is the only experimental study of this reaction to date. The preferred value is the geometric mean of the upper and lower limits (Mellouki et al., 1989), which are encompassed within the stated uncertainty factor. The Br-O₂ bond is very weak and the bond energy has been estimated by Blake et al. (1970) to be 4 kJ mol⁻¹. The product BrOO will therefore quickly decompose to yield Br+O₂.

References

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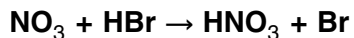
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III.A3.72



$$\Delta H^\circ = -60.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 1 \times 10^{-16}$	298	Mellouki et al., 1989	DF-EPR (a)
$(1.3 \pm 1.1) \times 10^{-16}$	298	Canosa-Mas et al., 1989	DF-A (b)

Comments

- (a) The rate coefficient was derived from fitting the measured data to a complex mechanism.
- (b) Discharge flow system with multipath absorption of NO_3 . The rate coefficient was derived from fitting the measured data to a complex mechanism.

Preferred Values

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

Comments on Preferred Values

The preferred value is the upper limit reported by Mellouki et al. (1989) in a study using the discharge flow-EPR technique. Canosa-Mas et al. (1989) reported a rate

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coefficient derived from fitting their data to a complex mechanism which, within the stated uncertainty limits, is consistent with the upper limit to the rate coefficient reported by Mellouki et al. (1989).

References

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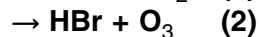
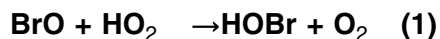
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III.A3.73



$$\Delta H^\circ(1) \geq -190 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -28 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.4 \pm 1.0) \times 10^{-11}$	300	Bridier et al., 1993	FP-UVA (a)
$4.77 \times 10^{-12} \exp[(580 \pm 100)/T]$	233–344	Larichev et al., 1995	DF-MS (b)
$(3.4 \pm 0.6) \times 10^{-11}$	303		
$2.5 \times 10^{-12} \exp[(520 \pm 80)/T]$	210–298	Elrod et al., 1996	DF-MS (c)
$(1.4 \pm 0.3) \times 10^{-11}$	298		
$3.13 \times 10^{-12} \exp[(536 \pm 206)/T]$	233–348	Li et al., 1997	DF-MS (d)
$(1.73 \pm 0.61) \times 10^{-11}$	298		(e)
$(2.05 \pm 0.64) \times 10^{-11}$	298		(f)
$(2.0 \pm 0.6) \times 10^{-11}$	298	Cronkhite et al., 1998	PLP-IR/UVA (g)
$9.4 \times 10^{-12} \exp[(345 \pm 60)/T]$	230–360	Bedjanian et al., 2001	DF-MS (h)
$(3.1 \pm 0.8) \times 10^{-11}$	298		
$(2.35 \pm 0.82) \times 10^{-11}$	298	Bloss et al., 2002	FP-UVA (a)

Comments

- (a) Photolysis of Br₂-O₃-Cl₂-CH₃OH-O₂-He mixtures. HO₂ and BrO radical concentrations were monitored by UV absorption spectroscopy under conditions where the HO₂ radical and BrO radical concentrations were of a similar magnitude.
- 5 (b) BrO radicals were generated by the O(³P)+Br₂ reaction, and their concentrations were monitored by MS in an excess of HO₂ radicals. A preliminary report of this study was noted in Poulet et al. (1992).
- (c) Turbulent flow system at 130 mbar total pressure. Reactant and product species were monitored by CIMS. BrO radicals were produced by the O(³P)+Br₂ reaction and HO₂ radicals by the H+O₂+M reaction. *k* was determined by monitoring the BrO radical concentrations in an excess of HO₂.
- 10 (d) BrO and HO₂ were monitored by MS. BrO radicals were produced by the Br+O₃ or O(³P)+Br₂ reactions and HO₂ radicals by the F+H₂O₂ or Cl+CH₃OH reactions. Experiments were carried out under conditions of both [BrO]≫[HO₂] and [HO₂]≫[BrO]. A similar temperature dependence of *k* was observed in each case, but values of *k* determined with excess BrO were systematically ~20% to 25% higher than those in excess HO₂.
- 15 (e) HO₂ in excess.
- (f) BrO in excess.
- 20 (g) Photolysis of Cl₂-CH₃OH-O₂-Br₂-O₃-N₂ mixtures. HO₂ and BrO radical concentrations were monitored simultaneously by infrared tunable diode laser absorption spectroscopy and UV absorption spectroscopy, respectively. Rate coefficients *k* were determined with [HO₂]≫[BrO].
- 25 (h) BrO radicals were produced by the Br+O₃ or O(³P)+Br₂ reactions and HO₂ radicals by the F+H₂O₂ reaction. Experiments were carried out under conditions

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of both $[\text{BrO}] \gg [\text{HO}_2]$ and $[\text{HO}_2] \gg [\text{BrO}]$. No systematic difference in the determined values of k was observed. Consistent values of k , measured relative to $k(\text{Br} + \text{HO}_2)$, were also reported.

Preferred Values

- 5 $k = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.5 \times 10^{-12} \exp(500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 210–360 K.

Reliability

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

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

10 *Comments on Preferred Values*

Disregarding the early study of Cox and Sheppard (1982) which gave a very low value for k , the reported rate coefficients at 298 K cover a range of just over a factor of two. This is despite the use of very similar techniques in some of the studies. The temperature dependence of k has generally provided values of E/R which are in good agreement, although that from the most recent temperature dependence study of Bedjanian et al. (2001) is substantially lower than three previous determinations.

15 The preferred value at 298 K is the mean of the rate coefficients of Bridier et al. (1993), Larichev et al. (1995), Elrod et al. (1996), Li et al. (1997), Cronkhite et al. (1998), Bedjanian et al. (2001) and Bloss et al. (2002) with substantial uncertainty limits. The preferred Arrhenius expression for k is obtained by taking the mean of the E/R values from the studies of Larichev et al. (1995), Elrod et al. (1996), Li et al. (1997) and Bedjanian et al. (2001), and combining it with a pre-exponential factor adjusted to give the preferred value of k at 298 K. The uncertainty in the preferred E/R value has been increased to encompass the recent result of Bedjanian et al. (2001).

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Several studies (Larichev et al., 1995; Elrod et al., 1996; Li et al., 1997; Bedjanian et al., 2001) have shown that the major product is HOBr. Larichev et al. (1995) and Bedjanian et al. (2001) were unable to obtain evidence for O₃ formation in their mass spectrometric studies of the reaction and set upper limits for the branching ratio of $k_2/k < 0.015$ and < 0.004 , respectively. From a study of the reverse reaction at above room temperature, Mellouki et al. (1994) have determined, by extrapolation, that the yield of HBr+O₃ is negligible ($< 0.01\%$) down to 200 K. Furthermore, k appears to be independent of pressure over the range covered by the studies to date of 1 mbar to 1 bar (Bridier et al., 1993; Larichev et al., 1995; Elrod et al., 1996; Li et al., 1997; Cronkhite et al., 2002) and there is no evidence for stable adduct formation. Thus all of the available data suggest that channel (1) is the sole pathway over the temperature range of the preferred values. This is supported by two recent theoretical studies (Guha and Francisco, 1992; Kaltsoyannis and Rowley, 2002) which conclude that the contribution of channel (2) is essentially zero.

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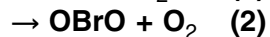
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$$\Delta H^\circ(1) = -151 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -99 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\sim 10^{-17}$	318–343	Rattigan et al., 1995	P-AS (a)
$k_2 = 7 \times 10^{-14} \exp[-(3100 \pm 350)/T]$	318–343		
$k_2 = 2.1 \times 10^{-18}$	298*		
$< (2.1 \pm 0.7) \times 10^{-17}$	298	Rowley et al., 1996	FP-AS (b)
$k_2 = (1.66 \pm 0.11) \times 10^{-18}$	298		

Comments

(a) Photolysis of $\text{Br}_2\text{-O}_3$ mixtures at 380 nm to 480 nm in N_2 or O_3 bath gas at total pressures in the range 16 mbar to 1000 mbar. Time-resolved UV absorption spectroscopy was used to monitor the concentrations of O_3 , Br_2 and BrO radicals before, during, and after irradiation. OBrO was also detected in absorption in the wavelength range 400 nm to 600 nm.

(b) Flash photolysis-longpath UV absorption technique. BrO radicals were produced by photolysis at ~ 400 nm of Br_2 in an excess of O_3 . Time-resolved UV/visible

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absorption spectra of BrO were recorded over the range 234 nm to 367 nm and of OBrO over the range 425 nm to 558 nm. The BrO decay was largely due to the BrO+BrO reaction but deviations from second-order behavior were observed at high O₃ concentrations, and attributed to the BrO+O₃ reaction. The upper limit was derived from an analysis of the [BrO] temporal profiles at high O₃ concentrations.

Preferred Values $k < 2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.*Comments on Preferred Values*

The two most recent studies of Rattigan et al. (1995) and Rowley et al. (1996) are in good agreement and set a lower upper limit to the rate coefficient for this reaction than did previous studies (Sander and Watson, 1981; Mauldin et al., 1993). The preferred upper limit to k at 298 K is therefore based on the results reported by Rattigan et al. (1995) and Rowley et al. (1996).

Previously, the reaction of BrO with O₃ had been assumed to occur exclusively by channel (1), but the positive identification of OBrO as a reaction product indicates that channel (2) is likely to be significant. The existing determinations of k_2 are in good agreement (Rattigan et al., 1995; Rowley et al., 1996) but involve significant uncertainties. Further studies are necessary before a branching ratio can be recommended.

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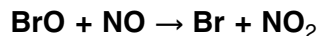
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$$\Delta H^\circ = -65 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.2 \pm 0.4) \times 10^{-11}$	298	Clyne and Watson, 1975	DF-MS (a)
$7.11 \times 10^{-12} \exp[(296 \pm 10)/T]$	230–425	Leu, 1979	DF-MS (a)
$(1.89 \pm 0.16) \times 10^{-11}$	298		
$1.28 \times 10^{-11} \exp[(181 \pm 46)/T]$	224–398	Watson et al., 1979	FP-UVA (b)
$(2.15 \pm 0.25) \times 10^{-11}$	298		
$(2.15 \pm 0.18) \times 10^{-11}$	298	Ray and Watson, 1981	DF-MS (a)

Comments

- (a) BrO radicals were produced by the $\text{O} + \text{Br}_2$ reaction and monitored by MS in an excess of NO.
- (b) BrO radicals were produced by the flash photolysis of $\text{Br}_2\text{-O}_2$ mixtures in the presence of an excess of NO. BrO radical concentrations were monitored by UV absorption at 339 nm. k was observed to be independent of pressure over the range 130 mbar to 930 mbar of He or N_2 .

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Preferred Values

$k = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 8.7 \times 10^{-12} \exp(260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–430 K.

Reliability

5 $\Delta \log k = \pm 0.1$ at 298 K.

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

Comments on Preferred Values

The results of the three low pressure mass spectrometric studies of Clyne and Watson (1975), Leu (1979) and Ray and Watson (1981) and the high pressure UV absorption study of Watson et al. (1979), all of which used pseudo-first order conditions, are in excellent agreement at 298 K and are considered to be more reliable than the earlier low pressure UV absorption study of Clyne and Cruse (1970). The results of the two temperature dependence studies (Leu, 1979; Watson et al., 1979) are in good agreement. The preferred Arrhenius expression is derived from a least-squares fit to all the data of Clyne and Watson (1975), Leu (1979), Watson et al. (1979) and Ray and Watson (1981). By combining the data reported in the high pressure UV absorption study (Watson et al., 1979) with those from the mass spectrometric studies (Clyne and Watson, 1975; Leu, 1979; Ray and Watson, 1981), this reaction does not exhibit any observable pressure dependence between 1 mbar and 1 bar total pressure. The temperature dependencies of the rate coefficients for the analogous ClO and HO₂ reactions are also negative and similar in magnitude.

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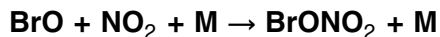
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$$\Delta H^\circ = -106 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.0 \pm 1.0) \times 10^{-31} [\text{N}_2]$	298	Sander et al., 1981	DF-MS/FP-UVA (a)
$(4.2 \pm 0.8) \times 10^{-31} (T/300)^{-2.0} [\text{O}_2]$	263–343	Danis et al., 1990	PLP-MS (b)
$5.4 \times 10^{-31} (T/298)^{-3.2} [\text{N}_2]$	248–346	Thorn et al., 1993	PLP-UVA (c)

Comments

(a) DF-MS study over the pressure range 1.3–8 mbar, and FP-UVA study from 57–933 mbar. In the DF-MS study, BrO radicals were produced by the reaction $\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$, and in the FP-UVA study BrO radicals were formed by the reaction of $\text{O}(^3\text{P})$ atoms (from the photolysis of O_2) with Br_2 . A major portion of the falloff curve was observed and analyzed with a fitted value of $F_c = 0.4$ at 298 K.

(b) BrO radicals were produced by the photolysis of O_3 at 248 nm in the presence of Br_2 . Rate coefficients were measured at total pressures below 16 mbar. Falloff curves were extrapolated using $F_c = \exp(-T/325)$.

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(c) BrO radicals were generated by the photolysis of Br₂-NO₂-N₂ mixtures at 351 nm, and were monitored by long-path (550 cm) absorption at 338.3 nm. The total pressure was varied over the range 21–1060 mbar. The data were analyzed with $F_c = \exp(-T/327)$, based on the fitted value of $F_c = 0.4$ of Sander et al. (1981).
5 If a value of $F_c = 0.6$ is used, a rate coefficient of $k_0 = 5.2 \times 10^{-31} (T/300)^{-3.2} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is obtained.

Preferred Values

$k_0 = 4.7 \times 10^{-31} (T/300)^{-3.1} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–350 K.

10 Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Values

15 The preferred values are based on the data of Sander et al. (1981), Danis et al. (1990) and Thorn et al. (1993). The reverse dissociation reaction $\text{BrONO}_2 + \text{M} \rightarrow \text{BrO} + \text{NO}_2 + \text{M}$ was measured by Orlando and Tyndall (1996) over the temperature range 320–340 K and at pressures of 133–1330 mbar. Their rate data were combined with the present preferred values for the reverse reaction leading to $\Delta H^\circ = -118 \text{ kJ} \cdot \text{mol}^{-1}$.
20 Ab initio calculations of the bond strength have also been reported by Rayez and Destriau (1993) and Parthiban and Lee (1998).

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High-pressure rate coefficients

Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.0 \pm 0.5) \times 10^{-11}$	298	Sander et al., 1981	DF-MS/FP-UVA (a)
$1.4 \times 10^{-11} (T/300)^{-1.2}$	248–346	Thorn et al., 1993	PLP-UVA (b)

Comments

- 5 (a) See comment (a) for k_0 . Extrapolation of falloff curve with a fitted value of $F_c=0.4$.
- (a) See comment (c) for k_0 . Evaluated with $F_c=\exp(-T/327)$. If $F_c=0.6$ is employed, $k_{\infty}=6.9 \times 10^{-12} (T/300)^{-2.9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is fitted.

Preferred Values

10 $k_{\infty} = 1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ independent of temperature over the range 240–350 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.1$ at 298 K.

$\Delta n = \pm 1$.

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Comments on Preferred Values

The preferred values are based on the data of Thorn et al. (1993) which are in good agreement with the data of Sander et al. (1981) at 298 K. A temperature-independent $F_c=0.4$ is used for representing the falloff curve which leads to the given practically
5 temperature-independent k_∞ .

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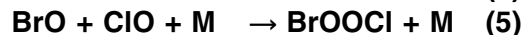
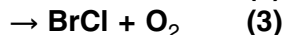
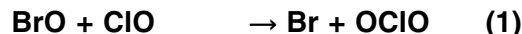
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$$\Delta H^\circ(1) = -14 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -12 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(3) = -207 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(4) = 52 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$6.1 \times 10^{-12} \exp[(240 \pm 60)/T]$ $(1.29 \pm 0.18) \times 10^{-11}$	220–400 298	Sander and Friedl, 1988	FP-UVA (a)
$4.7 \times 10^{-12} \exp[(320 \pm 60)/T]$ $(1.29 \pm 0.19) \times 10^{-11}$	220–400 298	Friedl and Sander, 1988	DF-MS (b)
$2.59 \times 10^{-12} \exp[(445 \pm 84)/T]$ $(1.08 \pm 0.20) \times 10^{-11}$	234–406 304	Turnipseed et al., 1991	DF-MS (c)
$k_1 = 6.7 \times 10^{-13} \exp[(622 \pm 94)/T]$	234–406		
$k_2 = 2.1 \times 10^{-12} \exp[(258 \pm 56)/T]$	234–406		
$k_3 = 1.9 \times 10^{-13} \exp[(513 \pm 86)/T]$	234–406		

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Branching Ratios</i>			
$k_1/k = 0.68 \pm 0.10$	220	Sander and Friedl, 1988	(a)
$k_1/k = 0.59 \pm 0.10$	298		
$k_1/k = 0.55 \pm 0.07$	220	Friedl and Sander, 1988	(b)
$k_1/k = 0.48 \pm 0.07$	298		
$k_1/k = 0.44 \pm 0.07$	400		
$k_2/k = 0.39 \pm 0.10$	220	Friedl and Sander, 1988	(b)
$k_2/k = 0.40 \pm 0.10$	298		
$k_2/k = 0.44 \pm 0.10$	400		
$k_3/k = 0.06 \pm 0.03$	220	Friedl and Sander, 1988	(b)
$k_3/k = 0.08 \pm 0.03$	298		
$k_3/k = 0.08 \pm 0.03$	400		
$k_1/k = 0.51 \pm 0.09$	250	Turnipseed et al., 1991	(c)
$k_1/k = 0.48 \pm 0.07$	304		
$k_1/k = 0.39 \pm 0.07$	406		
$(k_2 + k_3)/k = 0.46 \pm 0.7$	250	Turnipseed et al., 1991	(c)
$(k_2 + k_3)/k = 0.55 \pm 0.9$	304		
$(k_2 + k_3)/k = 0.61 \pm 0.11$	406		
$k_3/k = 0.10 \pm 0.02$	250	Turnipseed et al., 1991	(c)
$k_3/k = 0.09 \pm 0.02$	304		
$k_3/k = 0.09 \pm 0.02$	406		
$k_1/k = 0.53 \pm 0.05$	295	Bloss, 1999	(d)
$k_4/k < 0.02$	295		

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- (a) BrO, ClO and OCIO were detected using the temperature-dependent absorption cross-sections measured in the same study. BrO radical decays were monitored with $[\text{ClO}] > [\text{BrO}]$. Measurement of the rate coefficient ratio k_1/k was based on $\Delta[\text{OCIO}]/\Delta[\text{BrO}]$ as a function of time.
- (b) BrO, ClO, OCIO and BrCl were detected. BrO radical decays were measured in excess ClO. The branching ratios were based on the yields of OCIO, Cl (after conversion to BrCl) and BrCl compared to the amounts of BrO and ClO reacted.
- (c) Discharge flow system with MS detection of BrO, ClO, OCIO and BrCl. BrO radical decays were monitored in the presence of a 10- to 60-fold excess of ClO radicals. Branching ratios were based on the yields of OCIO, ClO and BrCl in the presence of the Cl atom scavengers HBr and $\text{C}_2\text{H}_3\text{Br}$.
- (d) Flash photolysis system with UV absorption detection (using a charge coupled detector) of BrO, ClO, OCIO and OBrO using differential absorption spectroscopy. The branching ratio k_4/k was based on the absence of characteristic OBrO absorption in the region 400 nm to 500 nm during the BrO and ClO decays.

Preferred Values

$k_1 = 6.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2 = 6.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_3 = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_1 = 1.6 \times 10^{-12} \exp(430/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–400 K.

$k_2 = 2.9 \times 10^{-12} \exp(220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–400 K.

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$k_3 = 5.8 \times 10^{-13} \exp(170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–400 K.

Reliability

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

5 $\Delta(E_1/R) = \Delta(E_2/R) = \Delta(E_3/R) = \pm 200$ K.

Comments on Preferred Values

The data base for this reaction is now extensive. Friedl and Sander (1989), using a discharge flow-mass spectrometry system, measured the overall rate coefficient over the temperature range 220–400 K and also over this temperature range determined
10 directly the branching ratios for the reaction channels producing BrCl and OCIO. In a separate study, the same authors (Sander and Friedl, 1989), using flash photolysis-ultraviolet absorption techniques, measured the overall rate coefficient over the temperature range 220–400 K and pressure range 67 mbar to 1000 mbar, and also determined the branching ratio for OCIO production at 220 K and 298 K. The results by these
15 two independent techniques (Friedl and Sander, 1989; Sander and Friedl, 1989) are in excellent agreement, with the overall rate coefficient showing a negative temperature dependence. The study of Turnipseed et al. (1991) also resulted in a comprehensive set of rate coefficient and branching ratio data. The overall rate coefficients from these three studies (Friedl and Sander, 1989; Sander and Friedl, 1989; Turnipseed
20 et al., 1991) are in good agreement at room temperature (within 20%) and are in excellent agreement at stratospheric temperatures. Toohey and Anderson (1988), using discharge flow-resonance fluorescence/LMR techniques, reported room temperature values of the overall rate coefficient and the branching ratio for OCIO production. They also found evidence for the direct production of BrCl in a vibrationally excited π state
25 (Toohey and Anderson, 1988). Poulet et al. (1990), using discharge flow-mass spectrometry techniques, reported room temperature values of the overall rate coefficient

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and branching ratios for OCIO and BrCl production. Clyne and Watson (1977) also studied this reaction using a discharge flow-MS system.

The results of the studies of Toohey and Anderson (1988), Sander and Friedl (1989), Friedl and Sander (1989), Poulet et al. (1990), Turnipseed et al. (1991) and Bloss (1999) are in reasonably good agreement. The rate coefficients of Hills et al. (1988), using a discharge flow-mass spectrometry technique, were independent of temperature over the range 241 K to 308 K and the room temperature rate coefficient was substantially lower than the average value from the above-mentioned studies (Friedl and Sander, 1989; Sander and Friedl, 1989; Turnipseed et al., 1991; Toohey and Anderson, 1988; Poulet et al., 1990). Hills et al. (1988) also reported no BrCl formation. In the flash photolysis study of Basco and Dogra (1971) a different interpretation of the reaction mechanism was used; the reported rate coefficients were low and are not used in the evaluation of the rate coefficient for this reaction.

The recommended Arrhenius expressions for the individual reaction channels are taken from the studies of Friedl and Sander (1989) and Turnipseed et al. (1991), which contain the most comprehensive sets of rate coefficient and branching ratio data. Both of these studies (Sander and Friedl, 1989; Turnipseed et al., 1991), as well as that of Sander and Friedl (1989), show that OCIO production by channel (1) becomes dominant at very low temperature. Both studies show an ~8% yield of BrCl by channel (3). The recommended expressions are consistent with the body of data from all studies except those of Hills et al. (1988) and Basco and Dogra (1971). Quantum mechanical calculations of the transition state configurations and energy minima on the P.E. surface for this reaction confirm the mechanism involving a BrOOCl peroxide intermediate (Papayannis et al., 2001).

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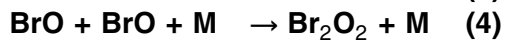
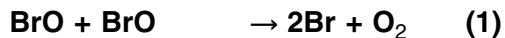
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$$\Delta H^\circ(1) = -16 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -209 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(3) = 24 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(4) = -59 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.17 \pm 0.67) \times 10^{-12}$	298	Clyne and Watson, 1975	DF-MS
$9.58 \times 10^{-13} \exp[(255 \pm 195)/T]$	223–388	Sander and Watson, 1981	(a)
$(2.17 \pm 0.68) \times 10^{-12}$	298		
$(3.2 \pm 0.5) \times 10^{-12}$	298	Lancar et al., 1991	(b)
$k_2 = (4.7 \pm 1.5) \times 10^{-13}$	298		
$(2.75 \pm 0.57) \times 10^{-12}$	298	Mauldin et al., 1993	(c)
$k_2 = (4.45 \pm 0.82) \times 10^{-13}$	298		
$k_1 = (2.49 \pm 0.42) \times 10^{-12}$	298	Rowley et al., 1996	(d)
$k_2 = (4.69 \pm 0.68) \times 10^{-13}$	298		
$(2.8 \pm 0.5) \times 10^{-12}$	298	Laszlo et al., 1997	(e)
$1.70 \times 10^{-12} \exp[(215 \pm 50)/T]$	204–388	Gilles et al., 1997	(f)
$(3.51 \pm 0.35) \times 10^{-12}$	298		
$k_1 = 5.31 \times 10^{-12} \exp[-(211 \pm 59)/T]$	250–298	Harwood et al., 1998	(g)
$k_2 = 1.13 \times 10^{-14} \exp[(983 \pm 111)/T]$	250–298		
$k_4 = (8.2 \pm 1.1) \times 10^{-32}[\text{M}]$	222		
<i>Branching Ratios</i>			
$k_1/k = 0.84 \pm 0.03$	298	Sander and Watson, 1981	(a)
$k_1/k = 0.84 \pm 0.01$	298	Mauldin et al., 1993	(c)
$k_1/k = 0.68 \pm 0.05$	220		
$k_1/k = 0.85 \pm 0.02$	298	Rowley et al., 1996	(d)

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- (a) Flash photolysis study with absorption spectroscopic detection of BrO radicals using the 7-0 band of the A-X system at 339 nm, for which a cross-section of $(1.14 \pm 0.14) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ was measured. The total pressure was 65 mbar to 789 mbar of N_2 . The branching ratio was determined from measurements with and without excess O_3 present, using two methods which gave the same result.
- (b) Discharge flow-mass spectrometry study, in which rate coefficients were determined from measurements with and without excess O_3 present. The rate coefficient, k_2 was obtained from BrO radical decays and Br_2 formation.
- (c) Flash photolysis-long path absorption technique. Measurements were made at 298 K and 220 K over a pressure range of 100 mbar to 800 mbar of He, N_2 and SF_6 . The overall rate coefficient was found to be independent of pressure at 298 K, but at 220 K to increase from $2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 133 mbar to $3.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 530 mbar. The branching ratio was found to be independent of pressure at 298 K and 220 K. An additional transient absorption feature was observed at 220 K and was tentatively attributed to Br_2O_2 . BrO concentrations were determined using the absorption cross-sections of Wahner et al. (1988) the cross-section at 338.5 nm was $1.71 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 298 K and $2.21 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 220 K (0.2 nm resolution). The following expressions were recommended for atmospheric modeling: $k_1 = 4.0 \times 10^{-12} \exp(-190/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_2 = 4.2 \times 10^{-14} \exp(660/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (d) Flash photolysis-UV absorption technique, with detection of BrO radicals using time-resolved CCD detection in the A-X system at 400 nm to 470 nm. BrO radical concentrations were determined using the absorption cross-sections of Wahner et al. (1988) compensated for the change in resolution. Rate coefficients were

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obtained from measurements with and without excess O_3 present. OBrO was observed in the presence of high concentrations of O_3 , apparently due to the BrO+ O_3 reaction and not to channel (3). The total pressure was 1000 mbar.

- (e) Pulsed laser photolysis of N_2O - Br_2 - N_2 mixtures, with absorption spectroscopic detection of BrO radicals. An absorption cross-section of $(1.41 \pm 0.15) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 338.5 nm was measured.
- (f) Pulsed laser photolysis of N_2O - Br_2 - N_2 mixtures, with absorption spectroscopic detection of BrO radicals. An absorption cross-section of $1.63 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 338.5 nm (0.5 nm resolution) was measured at 298 K. A similar temperature dependence of the absorption cross-section as observed by Wahner et al. (1988) was obtained.
- (g) Flash photolysis-absorption spectroscopy technique with detection of BrO radicals using time-resolved CCD detection in the A-X system at 400 nm to 470 nm. BrO concentrations were determined using the absorption cross-sections of Wahner et al. (1988) compensated for change in resolution and for temperature dependence. Rate coefficients were obtained from measurements with and without excess O_3 present. The total pressure was in the range 130 mbar to 1000 mbar. In the presence of O_3 and below 250 K, departure from second-order kinetics for BrO and a transient absorption attributed to Br_2O_2 was observed. The overall rate coefficient was pressure dependent in this temperature regime and the results were analyzed to yield a value for the rate coefficient for dimer formation [channel (4)] at 222 K. The formation of the dimer apparently replaced the bimolecular channels at low temperature, and the expressions for k_1 and k_2 only apply to temperatures $>250 \text{ K}$.

Preferred Values

$k_1 = 2.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–390 K.

$k_2 = 4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

5 $k = 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2 = 2.9 \times 10^{-14} \exp(840/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–390 K.

$k = 1.6 \times 10^{-12} \exp(210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–390 K.

Reliability

10 $\Delta \log k_1 = \Delta \log k_2 = \pm 0.1$ at 298 K.

$\Delta(E_1/R) = \Delta(E_2/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The total rate coefficient for the BrO+BrO reaction has been studied by a variety of techniques, including discharge flow-mass spectrometry and flash photolysis-ultraviolet absorption spectroscopy. The results from the latter technique depend on the value used for the absorption cross-section of BrO at the monitoring wavelength, usually 338.5 nm (the (7-0) band of the A←X transition). The absorption cross-section of BrO was remeasured by Gilles et al. (1997) with the values obtained being given by the expression $\sigma(\text{BrO}) = [3.29 - (5.58 \times 10^{-3})T] \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 338.5 nm. At a comparable resolution this expression gives values of $\sigma(\text{BrO}) \sim 10\%$ larger than those of Wahner et al. (1988) and employed by most of the earlier studies. When this difference is taken into account, the 298 K rate coefficients from the flash photolysis-absorption spectroscopy studies are in excellent agreement with the discharge flow studies (to within 10%), except for the study of Turnipseed et al. (1990). The mean
20 298 K rate coefficient is $3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ independent of pressure.
25

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The branching ratio between the bimolecular channels has been measured directly in the studies cited (Clyne and Watson, 1975; Mauldin et al., 1993; Rowley et al., 1996) and by Turnipseed et al. (1990) and indirectly by Jaffe and Mainquist (1980) from 258 K to 333 K, Cox et al. (1982) from 278 K to 348 K, and by Rattigan et al. (1995) at 298 K.

All studies are in agreement that $k_1/k=0.85\pm 0.03$ at 298 K and that the termolecular channel increases in importance with decreasing temperature. Recent ab initio calculations (Li and Jeong, 2001) have confirmed the existence of stable Br_2O_2 isomers and the endothermicity of channel (3) forming OBrO .

The temperature dependence is complicated by a pressure dependence of the rate coefficients at low temperatures (<250 K), as observed by Mauldin et al. (1993) and Harwood et al. (1998). The rate coefficients at <250 K increase with pressure, which Harwood et al. (1998) associated with the formation of an unstable Br_2O_2 dimer which was observed spectroscopically by both Mauldin et al. (1993) and Harwood et al. (1998). The study of Gilles et al. (1997), which covers the largest temperature range and was conducted at low total pressures, shows a small negative temperature dependence for the overall rate coefficient. The preferred values are based on the above 298 K rate coefficient of $k=3.2\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ and an $(E/R)=-210\text{ K}$, resulting in $k=1.6\times 10^{-12}\text{ exp}(210/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. The recommended channel-specific rate coefficients are based on the values of $k_1/k=0.85$ at 298 K and $k_1/k=0.68$ at 220 K.

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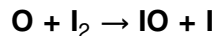
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Appendix 4: IO_x Reactions

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$$\Delta H^\circ = -89 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.38 \pm 0.44) \times 10^{-10}$	298	Ray and Watson, 1981	DF-MS (a)
$(1.4 \pm 0.4) \times 10^{-10}$	298	Laszo et al., 1995	PLP-AS (b)
$(1.3 \pm 0.15) \times 10^{-10}$	295	Hölscher et al., 1998	PLP-LIF (c)
$(1.2 \pm 0.1) \times 10^{-10}$	298	Tucceri et al., 2005	PLP-RF (d)

Comments

(a) MS detection of I₂ in a large excess of O(³P) atoms. The O(³P) atom concentrations were determined by titration with NO₂. The total pressure was ~2.6 mbar.

10 (b) O(³P) atoms were produced by pulsed laser photolysis of N₂O at 193 nm in the presence of I₂, at total pressures of ~260 mbar of N₂. The I₂ concentrations used were comparable to those of O(³P) atoms. The I₂ and IO radical concentrations were monitored simultaneously by absorption spectroscopy at 530 nm and at 340 nm to 435 nm, respectively, and values of *k* were derived by modeling the
15 I₂ and IO radical time-concentration profiles.

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(c) O(³P) atoms were produced by pulsed laser photolysis of N₂O at 193 nm in the presence of an excess of I₂, at total pressures of 40 mbar of N₃. IO radical concentrations were monitored by LIF at 445.05 nm.

(d) O(³P) atoms were produced by pulsed laser photolysis of NO₂ at 351 nm in the presence of an excess of I₂, which was monitored in situ at 500 nm. Total pressures of 80 or 266 mbar of He or 80 mbar N₂ were used. The I atom product was monitored by RF.

Preferred Values

$k = 1.25 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

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

Comments on Preferred Values

The recommended rate coefficient is based on the data of Hölscher et al. (1998) and Tucceri et al. (2005), both of whom employed sufficiently sensitive detection schemes that the IO self reaction was unimportant, and a simple exponential behaviour of IO and I was therefore observed. Note that the recommended value is within the large errors limits presented by Ray and Watson (1981) and Laszlo et al. (1995). The rate coefficient is large, approaching the gas kinetic collisional value and suggesting a near zero temperature dependence for k . This is in accord with the molecular beam study of the reaction by Parrish and Herschbach (1973).

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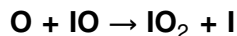
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$$\Delta H^\circ = -258 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.2 \pm 0.5) \times 10^{-10}$	298	Laszo et al., 1995	PLP-AS (a)
$(1.5 \pm 0.7) \times 10^{-10}$	298	Payne et al., 1998	DF-MS (b)
$(1.35 \pm 0.15) \times 10^{-10}$	296	Canosa-Mas et al., 1999	DF-RF (c)

Comments

- (a) $\text{O}(^3\text{P})$ atoms were produced by pulsed laser photolysis of N_2O at 193 nm in the presence of I_2 , at total pressures of ~ 260 mbar of N_2 . The I_2 concentrations used were comparable to those of $\text{O}(^3\text{P})$ atoms. The I_2 and IO radical concentrations were monitored simultaneously by absorption spectroscopy at 530 nm and at 340 nm to 435 nm, respectively, and values of k were derived by modeling the I_2 and IO radical time-concentration profiles.
- (b) IO radical concentrations were monitored by MS in the presence of a large excess of $\text{O}(^3\text{P})$ atoms. The total pressure was ~ 1.3 mbar of He.
- (c) IO radical concentrations in the presence of a large excess of $\text{O}(^3\text{P})$ atoms were monitored by conversion to I atoms by reaction with excess NO; the I atoms were observed by RF at 170–200 nm. The total pressure was ~ 2.5 mbar of He.

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Preferred Values

$k = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

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

5 *Comments on Preferred Values*

Prior to the three studies cited in the table (Laszlo et al., 1995; Payne et al., 1998; Canosa-Mas et al., 1999) only estimates of the rate coefficient for this reaction were available. The preferred value is the mean of the rate coefficients obtained by Laszlo et al. (1995), Payne et al. (1998) and Canosa-Mas et al. (1999), which are in good agreement and were obtained using quite different experimental techniques. The value of the rate coefficient is large, approaching the gas kinetic collisional value and suggesting a near zero temperature dependence of k .

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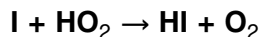
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III.A4.81



$$\Delta H^\circ = -94.9 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.47 \times 10^{-11} \exp[-(1090 \pm 130)/T]$	283–353	Jenkin et al., 1990	(a)
$(3.8 \pm 1.0) \times 10^{-13}$	298		

Comments

(a) Two experimental methods were used. The first technique involved a discharge flow system with EPR detection of I atoms (directly) and of HO₂ radicals after conversion to HO radicals (by reaction with NO). The first-order decays of HO₂ radicals in excess I atoms were measured, resulting in a rate coefficient of $k=(3.1\pm 1.2)\times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The second technique, which provided the temperature dependence, employed the molecular modulation method with UV absorption detection of HO₂ radicals, and with the I atom concentration being determined from the observed modulation of the I₂ absorption at 500 nm. Excess I atoms were employed, and the HO₂ radical self-reaction competed with the I+HO₂ reaction. The best analysis gave $k=(4.17\pm 0.4)\times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The Arrhenius expression was

obtained from the mean of the discharge flow and molecular modulation determinations at 298 K and the E/R obtained from a least-squares fit to the temperature-dependent data.

Preferred Values

- 5 $k = 3.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.5 \times 10^{-11} \exp(-1090/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 280–360 K.

Reliability

- $\Delta \log k = \pm 0.3$ at 298 K.
10 $\Delta (E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

- The preferred values are based on the two experimental studies reported by Jenkin et al. (1990) which are the only reported measurements for this reaction. The values of the rate coefficient at 298 K from the two studies agree quite well, although both
15 studies exhibited significant experimental error. The Arrhenius expression suggested by Jenkin et al. (1990) is accepted for the temperature dependence.

References

- Jenkin, M. E., Cox, R. A., Mellouki, A., Le Bras, G., and Poulet, G.: J. Phys. Chem.,
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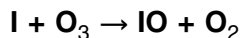
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$$\Delta H^\circ = -134 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

5

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.6 \pm 3.0) \times 10^{-13}$	303	Jenkin and Cox, 1985	MM-AS (a)
$(9.5 \pm 1.5) \times 10^{-13}$	298	Sander, 1986	FP-AS (b)
$2.3 \times 10^{-11} \exp[-(886 \pm 15)/T]$	231–337	Buben et al., 1990	DF-RF (c)
$(1.2 \pm 0.1) \times 10^{-12}$	298		
$2.3 \times 10^{-11} \exp[-(860 \pm 100)/T]$	240–370	Turnipseed et al., 1995	PLP-LIF (d)
$(1.38 \pm 0.08) \times 10^{-12}$	298		
$1.6 \times 10^{-11} \exp[-(750 \pm 194)/T]$	243–295	Hölscher et al., 1998	PLP-LIF (d)
$(1.2 \pm 0.1) \times 10^{-12}$	295		
$(1.28 \pm 0.06) \times 10^{-12}$	298	Tucceri et al., 2005	PLP-RF (c)

Comments

- (a) Modulated photolysis of $\text{I}_2\text{-O}_3$ mixtures at 570 nm and a total pressure of 34 mbar. IO radicals were monitored in absorption at 426.9 nm.
- (b) Detection of IO in absorption at 427.2 nm. A non-linear dependence of the pseudo first-order decay constant on the O_3 concentration was observed.

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(c) Direct detection of I atom reactant in excess O₃.

(d) Detection of IO product by LIF.

Preferred Values

$k = 1.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

5 $k = 2.1 \times 10^{-11} \exp(-830/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–370 K.

Reliability

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

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

10 *Comments on Preferred Values*

The most recent studies of this reaction (Buben et al., 1990; Turnipseed et al., 1995; Hölscher et al., 1998; Tucceri et al., 2005) are in excellent agreement and indicate somewhat higher rate coefficients than those obtained previously. A weighted average value of $(1.28 \pm 0.08) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is derived from these four studies, and
15 provides the basis of the recommendation.

The preferred Arrhenius expression for k is obtained by combining the mean of the values of E/R from the studies of Buben et al. (1990), Turnipseed et al. (1995) and Hölscher et al. (1998) with a pre-exponential factor adjusted to give the preferred value of k at 298 K.

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- Sander, S. P.: *J. Phys. Chem.*, 90, 2194, 1986.
- Tucceri, M. E., Dillon, T. J., and Crowley, J. N.: *Phys. Chem. Chem. Phys.*, 7, 1657, 2005.
- Turnipseed, A. A., Gilles, M. K., Burkholder, J. B., and Ravishankara, A. R.: *Chem. Phys. Lett.*, 242, 427, 1995.

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III.A4.83



$$\Delta H^\circ = -75.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.0 \pm 2.5) \times 10^{-33} (T/300)^{-1.0}$ [He]	320–450	van den Bergh and Troe, 1976	PLP-UVA (a)
$(1.6 \pm 0.5) \times 10^{-32}$ [N ₂]	330	van den Bergh et al., 1977	PLP-UVA (b)
$(9.5 \pm 3.0) \times 10^{-33}$ [Ar]	330		
$(1.05 \pm 0.30) \times 10^{-32}$ [Ar]	298		
$(1.03 \pm 0.06) \times 10^{-32} (T/300)^{-1.1}$ [He]	298–328	Basco and Hunt, 1978	FP (c)

Comments

(a) Photolysis of I₂ at 694 nm in the presence of NO and He. The pressure of He was varied between 1 and 200 bar. I₂ and INO spectra were observed.

(b) As in comment (a). The rate coefficient for M=Ar at 298 K was calculated from the measured rate coefficient at 330 K and the temperature dependence reported by van den Bergh and Troe (1976).

(c) Photolysis of I₂ in the presence of NO and Ar.

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Preferred Values

$k_0 = 1.8 \times 10^{-32} (T/300)^{-1.0} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290–450 K.

Reliability

- 5 $\Delta \log k_0 = \pm 0.1$ at 298 K.
 $\Delta n = \pm 0.5$ K.

Comments on Preferred Values

The preferred values are based on the rate coefficients for M=Ar determined by van den Bergh et al. (1976) and Basco and Hunt (1978) which agree remarkably well.

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High-pressure rate coefficients

Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\geq 1.7 \times 10^{-11}$	330	van den Bergh and Troe, 1976	PLP-UVA (a)

Comments

- 5 (a) As for comment (a) for k_0 . Based on a falloff extrapolation with $F_c=0.6$.

Preferred Values

$k_{\infty} = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 300–400 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.5$ over the temperature range 300–400 K.

10 *Comments on Preferred Values*

The preferred values are based on the only measurement by van den Bergh and Troe (1976), extrapolated by using a value of $F_c=0.6$.

References

- Basco, N. and Hunt, J. E.: Int. J. Chem. Kinet., 10, 733, 1978.
15 van den Bergh, H. and Troe, J.: J. Chem. Phys., 64, 736, 1976.

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III.A4.84



$$\Delta H^\circ = -79.8 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.5 \times 10^{-31} (T/300)^{-1.0} [\text{He}]$	320–450	van den Bergh and Troe, 1976	PLP-UVA (a)
$1.62 \times 10^{-31} [\text{He}]$	330	van den Bergh et al., 1977	PLP-UVA (b)
$2.6 \times 10^{-31} [\text{N}_2]$	330		
$(9.5 \pm 3.5) \times 10^{-32} [\text{He}]$	298	Mellouki et al., 1989	DF-EPR (c)
$3.1 \times 10^{-31} [\text{N}_2]$	298	Buben et al., 1990	FP-RF (d)

Comments

(a) Derived from the NO_2 catalyzed recombination of I atoms, with I atoms being produced by photolysis of I_2 at 694 nm. The falloff curve was measured from 1–200 bar of He, and only a short extrapolation to k_0 was required.

(b) As in comment (a). The efficiencies of 26 bath gases were studied.

(c) Measurements performed over the pressure range 0.8 to 2.9 mbar.

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(d) I atoms generated by photolysis of CH₃I in a flow system with NO₂-N₂ mixtures. The bath gases N₂, O₂, Ar and He were studied at total pressures between 0.7 and 13 mbar.

Preferred Values

5 $k_0 = 3.0 \times 10^{-31} (T/300)^{-1.0} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290–450 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 298 K.

$\Delta n = \pm 1$ K.

10 *Comments on Preferred Values*

The preferred values are based on the results of the studies of van den Bergh and Troe (1976), van den Bergh et al. (1977) and Buben et al. (1990). The data of Mellouki et al. (1989) for M=He are also consistent with these data. Falloff extrapolations are made with a fitted value of $F_c=0.63$ from van den Bergh and Troe (1976).

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High-pressure rate coefficients

Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
6.6×10^{-11}	320–350	van den Bergh and Troe, 1976	PLP-UVA (a)

5 Comments

(a) See comment (a) for k_0 . Extrapolation of the falloff curve towards the high pressure limit uses a fitted value of $F_c=0.63$.

Preferred Values

10 $k_{\infty} = 6.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 290–450 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.3$ over the temperature range 300–400 K.

Comments on Preferred Values

15 The preferred values are based on the results of the study of van den Bergh and Troe (1976). Falloff curves are represented with $F_c=0.63$.

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5 Mellouki, A., Laverdet, G., Jourdain, J. L., and Poulet, G.: Int. J. Chem. Kinet., 21, 1161, 1989.

van den Bergh, H. and Troe, J.: J. Chem. Phys., 64, 736, 1976.

van den Bergh, H., Benoit-Guyot, N., and Troe, J.: Int. J. Chem. Kinet., 9, 223, 1977.

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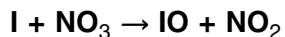
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III.A4.85



$$\Delta H^\circ = -31.4 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.5 \pm 1.9) \times 10^{-10}$	298	Chambers et al., 1992	DF-RF (a)

Comments

(a) Discharge flow system with resonance fluorescence detection of I atoms in the presence of excess NO_3 radicals. NO_3 radicals and I atoms were produced by the $\text{F} + \text{HNO}_3$ and $\text{O} + \text{I}_2$ reactions, respectively. NO_3 radical concentrations were measured by visible absorption spectroscopy. Corrections of up to 33% were applied to compensate for diffusion effects.

Preferred Values

No recommendation.

Comments on Preferred Values

The only reported measurement of this rate constant was made using the discharge flow technique at room temperature (Chamber et al., 1992). Difficulties were encoun-

tered due to wall reactions, and the pseudo first-order plots exhibited pronounced curvature at contact times longer than 3 ms. In their study of HI+NO₃, Lancar et al. (1991) stated that they failed to observe a reaction between I atoms and NO₃ radicals, but gave no details or an upper limit. In view of these uncertainties, no recommendation is made for the rate coefficient at this time.

References

Chambers, R. M., Heard, A. C., and Wayne, R. P.: J. Phys. Chem., 96, 3321, 1992.
Lancar, I. T., Mellouki, A., and Poulet, G.: Chem. Phys. Lett., 177, 554, 1991.

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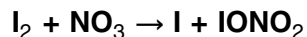
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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.5 \pm 0.5) \times 10^{-12}$	292–423	Chambers et al., 1992	(a)

Comments

(a) Discharge flow system with simultaneous fluorescence detection of I_2 and visible absorption spectroscopic measurement of NO_3 radicals. NO_3 radicals were produced by the $\text{F} + \text{HNO}_3$ reaction. Pseudo first-order conditions were used with NO_3 radical concentrations in excess over I_2 . Experiments were performed to substantiate that I_2 loss was due to reaction with NO_3 radicals, and small corrections were made to compensate for diffusion effects; the overall error takes into account the uncertainties in the NO_3 radical concentrations ($\pm 26\%$).

Preferred Values

No recommendation.

Comments on Preferred Values

There is only one reported measurement of this rate constant (Chambers et al., 1992) and the products of the reaction were not determined. Chambers et al. (1992)

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argue that product channels giving $I+IO+NO_2$, $I+O_2+INO$ or $IO+INO_2$ are all endothermic and can be ruled out, and propose formation of $I+IONO_2$. If this is correct, the high value of $1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the rate coefficient implies an exothermic process and thus an upper limit of $\sim 29 \text{ kJ mol}^{-1}$ for $\Delta H^\circ(IONO_2)$. The calculated (ab initio) bond dissociation energy $D_0(IO-NO_2)=132 \text{ kJ mol}^{-1}$ of Rayez and Destriau (2002) can be combined with formation enthalpies of IO (116 kJ mol^{-1}) and NO_2 (33 kJ mol^{-1}) to give $\Delta H^\circ(IONO_2)=17 \text{ kJ mol}^{-1}$ which would make the reaction, as written, exothermic. On the other hand, the RRKM analysis of the fall-off curves for $IO+NO_2$ /ab-initio calculations of Allan and Plane (1993) indicate that $\Delta H^\circ(IONO_2)=70 \pm 16 \text{ kJ mol}^{-1}$. This would render the reaction significantly endothermic. For this reason we make no recommendation.

References

- Allan, B. J. and Plane, J. M. C.: J. Phys. Chem. A., 106, 8634, 2002.
Chambers, R. M., Heard, A. C., and Wayne, R. P.: J. Phys. Chem., 96, 3321, 1992.
Rayez, M. T. and Destriau, M.: Chem. Phys. Lett., 206, 278, 1993.

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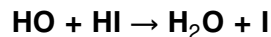
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III.A4.87



$$\Delta H^\circ = -198.8 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

5

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.3 \pm 0.5) \times 10^{-11}$	295	Takacs and Glass, 1973	DF-EPR
$(2.7 \pm 0.2) \times 10^{-11}$	298	Mac Leod et al., 1990	PLP-RF
$(3.3 \pm 0.2) \times 10^{-11}$	298	Lancar et al., 1991	DF-EPR
$(7.0_{-0.4}^{+1.9} \times 10^{-11} (T/298)^{-(1.5 \pm 0.5)})$	246–353	Campuzano-Jost and Crowley, 1999	PLP-RF
$(6.5_{-0.4}^{+2.0}) \times 10^{-11}$	294		

Preferred Values

$k = 7.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.6 \times 10^{-11} \exp(440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–360 K.

10

Reliability

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

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

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The preferred values are based on the most recent and extensive study of Campuzano-Jost and Crowley (1999), in which, although the HI concentrations in the reaction cell were not monitored directly during the experiments, care was taken to remove potential impurities in the HI and a number of HO radical precursors were investigated before choosing H₂O₂ photolysis at 248 nm as the optimum. Additionally, two analyses using ion chromatography showed that the HI concentrations in the reaction cell were within ~20% to 25% of those expected (Campuzano-Jost and Crowley, 1999). The lower room temperature rate coefficients obtained in the studies of Mac Leod et al. (1990) and Lancar et al. (1991), which are more than a factor of two higher than the earlier results of Takacs and Glass (1973), may have suffered from unrecognized losses of HI due to reactions with the HO radical precursors used and/or (in the study of Lancar et al., 1991) from generation of vibrationally-excited HO radicals (Campuzano-Jost and Crowley, 1999).

References

- Campuzano-Jost, P. and Crowley, J. N.: J. Phys. Chem. A, 103, 2712, 1999.
Lancar, I. T., Mellouko, A., and Poulet, G.: Chem. Phys. Lett., 177, 554, 1991.
Mac Leod, H., Balestra, C., Jourdain, J. L., Laverdet, G., and Le Bras, G.: Int. J. Chem. Kinet., 22, 1167, 1990.
Takacs, G. A. and Glass, G. P.: J. Phys. Chem., 77, 1948, 1973.

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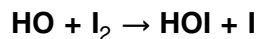
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III.A3.88



$$\Delta H^\circ = -62.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.6_{-0.8}^{+1.6}) \times 10^{-10}$	298	Loewenstein and Anderson, 1985	DF-RF
$(2.1 \pm 0.6) \times 10^{-10}$	240–348	Gilles et al., 1999	PLP-LIF (a)
<i>Relative Rate Coefficients</i>			
$(2.3 \pm 0.3) \times 10^{-10}$	294	Jenkin et al., 1984	RR (b)

Comments

- (a) From measurements of the rate coefficients at 240 K, 293–295 K and 348 K, a least-squares analysis led to $k = 1.97 \times 10^{-10} \exp[(21 \pm 318)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The temperature independent expression cited in the table is preferred (Gilles et al., 1999)
- (b) Steady-state photolysis of HONO-I₂-ethene-air (or N₂) mixtures at 1 bar total pressure. A rate coefficient ratio $k(\text{HO}+\text{I}_2)/k(\text{HO}+\text{ethene}) = 26.5 \pm 3.5$ was obtained from the rate of disappearance of ethene as a function of the I₂ concentration. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{HO}+\text{ethene}) = 8.69 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 294 K and 1 bar of air (Atkinson, 1997).

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Preferred Values

$k = 2.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 240–350 K.

Reliability

- 5 $\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

10 The reported room temperature rate coefficients of Loewenstein and Anderson (1985), Jenkin et al. (1984) and Gilles et al. (1999) agree well, noting the large quoted error limits associated with the Loewenstein and Anderson (1985) data. The preferred values are based on the most recent and extensive study of Gilles et al. (1999). Loewenstein and Anderson (1985) determined that the exclusive products are HOI and I.

References

- 15 Atkinson, R.: J. Phys. Chem. Ref. Data, 26, 215, 1997.
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Jenkin, M. E., Clemitshaw, K. C., and Cox, R. A.: J. Chem. Soc. Faraday Trans., 2, 80, 1633, 1984.
20 Loewenstein, L. M. and Anderson, J. G.: J. Phys. Chem., 89, 5371, 1985.

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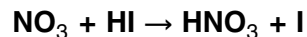
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III.A4.89



$$\Delta H^\circ = -128.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.3 \times 10^{-12} \exp[-(1830 \pm 300)/T]$	298–373	Lancar et al., 1991	DF-EPR/MS (a)
$(2.5 \pm 0.8) \times 10^{-15}$	298		

Comments

(a) NO_3 radicals were generated by the reaction of F atoms with HNO_3 . The rate coefficient was determined by measuring the decay rate of NO_3 radicals (by MS, correcting for the contribution of HNO_3 to the $m/z=62$ ion signal) or by measuring the formation rate of I atoms (by EPR).

Preferred Values

No recommendation.

Comments on Preferred Values

Although the rate coefficients measured in the only study (Lancar et al., 1991) of this reaction from the decay of NO_3 using MS and I atom production using

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EPR spectrometry were in agreement (Lancar et al., 1991), there is a serious potential for secondary chemistry occurring in the system leading to an overestimation of the rate coefficient for the elementary process. Lancar et al. (1991) reported that the reaction of $I+NO_3 \rightarrow IO+NO_2$ does not occur, while Chambers et al. (1992) observed that the $I+NO_3$ reaction is rapid, with a measured rate coefficient of $k(I+NO_3)=4.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, and that I atoms are regenerated from subsequent reactions of IO radicals. Until this uncertainty is resolved, no recommendation can be made.

References

- 10 Chambers, R. M., Heard, A. C., and Wayne, R. P.: J. Phys. Chem., 96, 3321, 1992.
Lancar, I. T., Mellouki, A., and Poulet, G.: Chem. Phys. Lett., 177, 554, 1991.

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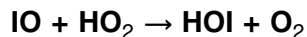
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$$\Delta H^\circ = -200 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.4 \pm 0.7) \times 10^{-11}$	298	Jenkin et al., 1991	MM (a)
$(1.03 \pm 0.13) \times 10^{-10}$	298	Maguin et al., 1992	DF-MS (b)
$9.3 \times 10^{-12} \exp[(680 \pm 110)/T]$	274–373	Cronkhite et al., 1999	FP-UVA/IR (c)
$(9.7 \pm 2.9) \times 10^{-11}$	298		
$(7.1 \pm 1.6) \times 10^{-11}$	296	Canosa-Mas et al., 1999	DF-RF (d)
$2.2 \times 10^{-11} \exp[(400 \pm 80)/T]$	273–353	Knight and Crowley, 2001	DF-MS (e)
$(8.9 \pm 0.9) \times 10^{-11}$	298		(f)
$(8.00 \pm 0.15) \times 10^{-11}$	298		(g)

Comments

(a) Molecular modulation technique with UV absorption detection of HO₂ radicals at 220 nm and visible absorption detection of IO radicals at 427 nm. The radicals were produced by photolysis of O₃-CH₃OH-I₂-O₂ mixtures at 254 nm with HO₂ in excess over IO. The rate coefficient, *k*, was derived from a non-linear least-squares analysis of absorption wave-forms. The error limits do not include possible systematic errors.

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(b) Discharge flow system with MS detection of HO₂ and IO radicals and HOI. IO and HO₂ radicals were produced by the O(³P)+I₂ and Cl+CH₃OH+O₂, reactions, respectively. Pseudo first-order decays of IO radicals were measured in the presence of excess HO₂. The cited value of *k* is the average of 25 experiments. HOI was shown to be a major product. The uniqueness of the HOI+O₂ forming channel could not be established, although no evidence was found for O₃ formation by the alternative HI+O₃ channel.

(c) Pulsed laser photolysis of Cl₂-CH₃OH-O₂-I₂-NO₂-SF₆-N₂ mixtures at 308 nm with simultaneous time-resolved detection of HO₂ radicals (by infrared TDLS) and IO radicals (by visible absorption spectroscopy). HO₂ radicals were generated by the reaction of Cl atoms (from photolysis of Cl₂) with CH₃OH in the presence of O₂, and IO radicals were generated by the reaction of O(³P) atoms (from photolysis of NO₂) with I₂.

(d) IO generated from O(³P)+CF₃I (following discharge of O₂). HO₂ generated from Cl+CH₃OH in the presence of O₂. IO and HO₂ concentrations were monitored by titration to I and OH by the respective reactions with NO. Experiments carried out at 1.7–2 Torr.

(e) IO generated from O(³P)+CF₃I or O(³P)+I₂ (following discharge of O₂). HO₂ generated from Cl+CH₃OH in the presence of O₂. IO and HO₂ concentrations were monitored directly at their parent peaks. Experiments carried out at 1.3–2.3 mbar.

(f) IO from O(³P)+CF₃I.

(g) IO from O(³P)+I₂.

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Preferred Values

$k = 8.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.4 \times 10^{-11} \exp(540/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–380 K.

Reliability

5 $\Delta \log k = \pm 0.2$ at 298 K.

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

Comments on Preferred Values

The preferred value at 298 K is the average of the reported room temperature data (Jenkin et al., 1991; Maguin et al., 1992; Cronkhite et al., 1999; Canosa-Mas et al., 1999; Knight and Crowley, 2001). The preferred Arrhenius expression is based on the E/R values from the temperature dependence studies of Cronkhite et al. (1999) and Knight and Crowley (2001), combined with a pre-exponential factor adjusted to give the preferred value of k at 298 K.

15 The studies of Maguin et al. (1992) and Knight and Crowley (2001) provide strong evidence that the formation of HOI and O₂ is the dominant pathway. On the basis of current thermochemical data for the IO radical, the channel forming HI+O₃ is endothermic by $\sim 40 \text{ kJ mol}^{-1}$, and a limit of $\leq 10\%$ has been reported for this channel (Knight and Crowley, 2001), based on no detectable formation of O₃. As pointed out by Knight and Crowley (2001), a channel forming OH+OIO is exothermic by 12 kJ mol^{-1} , but no firm evidence for this channel has been reported.

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Knight, G. P. and Crowley, J. N.: Phys. Chem. Chem. Phys., 3, 393, 2001.

5 Maguin, F., Laverdet, G., Le Bras, G., and Poulet, G.: J. Phys. Chem., 96, 1775, 1992.

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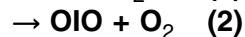
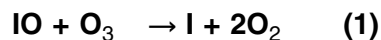
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III.A4.91



$$\Delta H^\circ = -151 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_1 < 1.2 \times 10^{-15}$	292	Larin et al., 1999	F-RF (a)
$k_2 < 2.3 \times 10^{-16}$	323		

Comments

(a) I atoms were generated by photolysis of CF_3I at 253.7 nm in a fast flow system using He as the carrier gas. Channel (1) was investigated by direct monitoring of I atom concentrations by resonance fluorescence and channel (2) was studied by monitoring the IO concentration by addition of NO and detection of the I atoms generated.

Preferred Values

$$k_1 < 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 < 2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

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Comments on Preferred Values

The only experimental study of the reaction (Larin et al., 1999) gives upper limits for the rate coefficients for the two channels which are substantially higher than the corresponding rate coefficients for the analogous reactions of FO, ClO, and BrO radicals.

5 It is likely that the rate coefficients are substantially smaller but the measured upper limits are provisionally accepted.

References

Larin, K., Nevozhai, D. V., Spasskii, A. I., Trofimova, E. F. M., and Turkin, L. E.: Kinet. Katal., 40, 487, 1999, Eng. Trans. p. 435.

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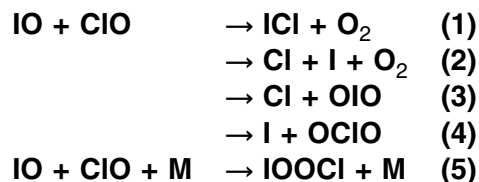
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III.A4.92



$$\Delta H^\circ(1) = -200 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = 10 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(3) = -19 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(4) = -15 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.1 \pm 0.2) \times 10^{-11}$	298	Bedjanian et al., 1997	DF-MS (a)
$5.1 \times 10^{-12} \exp[(280 \pm 80)/T]$	200–362	Turnipseed et al., 1997	(b)
$(1.29 \pm 0.27) \times 10^{-11}$	298		
<i>Branching Ratio</i>			
$k_1/k = 0.20 \pm 0.02$	298	Bedjanian et al., 1997	(c)
$k_2/k = 0.25 \pm 0.02$	298		
$k_4/k = 0.55 \pm 0.03$	298		
$(k_1 + k_3)/k = 0.14 \pm 0.04$	298	Turnipseed et al., 1997	(d)

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Comments

- (a) The rate coefficient k was determined from the decay of IO radicals in the presence of excess ClO under pseudo-first order conditions. The total pressure was 1.3 mbar He. k was measured in four different reaction mixtures using CF₃I and I₂ as sources of IO radicals, and OCIO and Cl₂O as sources of ClO radicals.
- (b) Coupled DF-PLP system with LIF detection of IO radicals. IO radicals were photolytically generated in excess ClO, which was measured by UV absorption. The temporal profile of IO allowed accurate determination of k . I atoms were a major product, with a yield of 0.8 ± 0.2 at 298 K. Total pressure was 6.6 mbar to 21 mbar of N₂-He. The quoted errors include estimates of systematic errors.
- (c) Quantitative detection of reaction products OCIO, Cl and ICl, using both absolute and relative rate approaches to determine the branching ratios. The errors quoted are two least-squares standard deviations.
- (d) Based on the ratio of the overall bimolecular rate coefficient determined from the first-order decay of IO in excess ClO (giving $k_1 + k_3$) with 4×10^{15} molecule cm⁻³ of O₃ present, to the total rate coefficient k determined in a similar manner with no excess O₃ present. At 223 K the yield of I atoms was 0.78 ± 0.25 , suggesting that the I atom yield does not vary significantly with temperature over the range 223 K to 298 K.

Preferred Values

$k = 1.2 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

$k = 4.7 \times 10^{-12} \exp(280/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 200–370 K.

$k_1/k = 0.20$ at 298 K.

$k_2/k = 0.25$ at 298 K.

$k_4/k = 0.55$ at 298 K.

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Reliability

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

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

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

5 $\Delta (k_2/k) = 0.10$ at 298 K.

$\Delta (k_4/k) = 0.10$ at 298 K.

Comments on Preferred Values

The two experimental studies of Bedjanian et al. (1997) and Turnipseed et al. (1997), which used different techniques, give overall rate coefficients k which are in excellent
10 agreement at 298 K. The recommended value is a simple mean of the two results (Bedjanian et al., 1997; Turnipseed et al., 1997). The temperature dependence from Turnipseed et al. (1997) is consistent with those observed for other exothermic XO+YO reactions and is accepted for the recommendation.

The quantitative information from the two studies (Bedjanian et al., 1997; Turnipseed et al., 1997) concerning the product channels is consistent within the cited
15 uncertainties, with the discharge flow study of Bedjanian et al. (1997) giving more detailed data and being used for the recommendation. The overall rate coefficient is accounted for by Reactions (1)+(2)+(4) and it is concluded that Reaction (3) is negligible. Provisionally, the branching ratios at 298 K can be applied to stratospheric
20 temperatures since the I atom yield exhibits no significant temperature dependence (Turnipseed et al., 1997).

References

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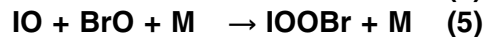
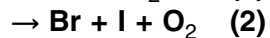
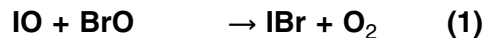
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III.A4.93



$$\Delta H^\circ(1) = -195 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -17 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(3) = -47 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(4) = 23 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.9 \pm 2.7) \times 10^{-11}$	298	Laszlo et al., 1997	PLP-AS (a)
$k_1 + k_3 = 2.5 \times 10^{-11} \exp[(260 \pm 100)/T]$	204–388	Gilles et al., 1997	PLP-LIF (b)
$k_1 + k_3 = 6.0 \times 10^{-11}$	298		
$(8.5 \pm 1.5) \times 10^{-11}$	298	Bedjanian et al., 1998	DF-MS (c)
$k_1 + k_3 = (7.5 \pm 1.0) \times 10^{-11}$	298		
$6.7 \times 10^{-12} \exp[(760 \pm 30)/T]$	210–333	Rowley et al., 2001	(d)
$(8.5 \pm 1.4) \times 10^{-11}$	295		
<i>Branching Ratios</i>			
$(k_2 + k_4)/k < 0.35$	298	Gilles et al., 1997	(b)
$k_1/k < 0.05$	298	Bedjanian et al., 1998	(e)
$k_2/k < 0.3$	298		
$k_3/k = 0.65\text{--}1.0$	298		
$k_4/k < 0.2$	298		
$(k_2 + k_4)/k < 0.3$	298		
$k_1/k < 0.2$	298	Rowley et al., 2001	(f)
$k_4/k < 0.15$	298		

Comments

- 5 (a) IO and BrO radicals were monitored at 427.2 nm and 338.5 nm, respectively, using resolutions of 0.3 nm and 0.6 nm and cross-sections of $2.8 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$

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and $1.4 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$, respectively. The rate coefficient k was determined by a computer fit to complex kinetic decay curves. The total pressure was 260 mbar.

- (b) IO radicals were detected by LIF. Pseudo-first order decays of IO radicals were measured in the presence of excess BrO and O₃. The reported rate coefficient applies only to the non-I-atom producing channels. An upper limit of 0.35 is suggested for the fraction of the overall reaction yielding I atoms at 298 K. Total pressure was 8 mbar to 20 mbar.
- (c) IO radical decays were monitored in the presence of excess BrO and O₃ to obtain the rate coefficient for the total non-I-atom forming channels. The total rate coefficient was obtained from simulations of the BrO, IO and IBr profiles. The total pressure was 1 mbar.
- (d) Pulsed laser photolysis with absorption spectroscopic detection of BrO and IO radicals using a time-resolved charge coupled detector (CCD) in the A-X systems at 300 nm to 350 nm and 400 nm to 470 nm, respectively. The IO radical cross-section at 427.2 nm was measured to be $(1.9 \pm 0.17) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ (1.13 nm resolution) and the BrO radical differential cross-sections were based on those measured by Wahner et al. (1988), but increased in magnitude by 9% as recommended by Gilles et al. (1997) and adjusted for a resolution of 1.13 nm. The rate coefficient k was determined by computer simulation of IO decays in excess BrO₂. The total pressure was 100 mbar to 1000 mbar.
- (e) Several experiments under varying conditions in the discharge flow system were used to establish the branching ratios. The major channel produces Br+OIO with a branching ratio in the range given. Only upper limits were obtained for I atom and IBr formation.
- (f) Based on the upper limits to the formation of the products IBr and OBrO, as measured by absorption spectroscopy. OIO was shown to be the major product.

Preferred Values

$k = 8.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.5 \times 10^{-11} \exp(510/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–390 K.

$k_3/k = 0.80$ at 298 K.

5 Reliability

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

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

$\Delta (k_3/k) = 0.15$ at 298 K.

Comments on Preferred Values

10 The kinetic studies of this reaction by Laszlo et al. (1997), Gilles et al. (1997), Bedjanian et al. (1998) and Rowley et al. (2001) are in remarkably good agreement considering the experimental difficulties. Both Gilles et al. (1997) and Bedjanian et al. (1998) observed first-order kinetics for IO radical decays in excess BrO to obtain the rate coefficient for non-I-atom producing channels,

15 $(k_1+k_3)=(6.8\pm 0.8)\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The overall rate coefficients measured by Bedjanian et al. (1998) and Rowley et al. (2001) which were measured under complex kinetic conditions, are nevertheless in excellent agreement, giving $k=(8.5\pm 1.2)\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These measurements give a value of

20 $(k_1+k_3)/k=0.80\pm 0.15$ which lies in the middle of the range suggested by Bedjanian et al. (1998) for the branching ratio k_3/k . Considering that the IBr measurements of Bedjanian et al. (1998) give $k_1/k < 0.05$, we recommend that $k_3/k=0.80$ and that the total rate coefficient is that determined by Bedjanian et al. (1998) and Rowley et al. (2001) at 298 K. The rate coefficient measurement of Laszlo et al. (1997) is less precise but agrees within the experimental error limits with the recommendation.

25 The two studies of the temperature dependence (Gilles et al., 1997; Rowley et

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al., 2001) both show a negative activation energy for this radical + radical reaction. Although the temperature dependence of Gilles et al. (1997) is derived from measurements of k_1+k_3 over a wider temperature range, their result may not reflect the temperature dependence of the overall reaction if the branching ratio changes with temperature. The recommended temperature dependence is the simple mean of the two determinations of Gilles et al. (1997) and Rowley et al. (2001) with the pre-exponential factor, A , being adjusted to fit the preferred 298 K rate coefficient. The data do not allow a precise recommendation for the remaining branching between channels (1), (2) and (4). However, OBrO formation is not favorable on thermochemical grounds.

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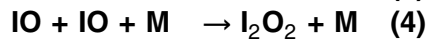
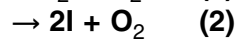
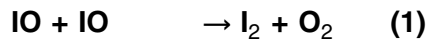
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$$\Delta H^\circ(1) = -170 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -18 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(3) = -48 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.0 \pm 1.8) \times 10^{-11}$	298	Laszlo et al., 1995	(a)
$(9.9 \pm 1.5) \times 10^{-11}$	250–320	Harwood et al., 1997	(b)
$(1.0 \pm 0.3) \times 10^{-10}$	295	Atkinson et al., 1999	(c)
$(9.3 \pm 1.0) \times 10^{-11}$	295	Ingham et al., 2000	(d)
$4.54 \times 10^{-11} \exp[(182 \pm 122)/T]$	250–320	Bloss et al., 2001	(e)
$(8.2 \pm 1.0) \times 10^{-11}$	298		
$(9.3 \pm 1.0) \times 10^{-11}$	296	Vipond, 2002	(f)
<i>Branching Ratios</i>			
$k_1/k < 0.05$	298	Sander, 1986	(g)
$(k_2 + 0.5k_3)/k = 0.45$ at 28 mbar	298		
$(k_2 + 0.5k_3)/k = 0.18$ at 870 mbar	298		
$k_1/k < 0.05$	298	Laszlo et al., 1995	(a)
$(0.5k_3 + k_4)/k = 0.78$ at 1 bar	298	Harwood et al., 1977	(h)
$k_1/k < 0.30$	298		
$k_1/k < 0.05$	298	Bloss et al., 2001	(i)
$k_2/k = 0.11 \pm 0.04$	298		
$k_3/k = 0.38 \pm 0.08$	298		
$k_4/k = 0.46 \pm 0.06$	298		
$k_2/k = 0.56 \pm 0.20$	296	Vipond, 2002	(f)

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- 5 (a) Pulsed laser photolysis with detection of IO radicals by absorption spectroscopy using the 4-0 band of the A-X system at 427.2 nm, for which a cross-section of $(2.8 \pm 0.5) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ was measured. The total pressure was 78 mbar to 789 mbar of N_2 . No prompt I_2 formation from IO decay was observed.
- 10 (b) Pulsed laser photolysis with detection of IO radicals by absorption spectroscopy using the 4-0 band of the A-X system at 427.2 nm, for which a temperature-independent cross-section of $(3.6 \pm 0.5) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ was measured. The total pressure was 78 mbar to 789 mbar of N_2 . No statistically significant temperature dependence of either k or σ was observed over the temperature range studied.
- 15 (c) Pulsed laser photolysis with detection of IO radicals by cavity ring-down spectroscopy using the 2-0 bandhead of the A-X system at 445.02 nm, for which an absorption cross-section of $(7.3 \pm 0.7) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ was used. This was determined relative to $\sigma = (3.6 \pm 0.7) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ measured by Harwood et al. (1997). The total pressure was 12.4 mbar to 40.2 mbar of Ar.
- 20 (d) Pulsed laser photolysis (248 nm) of $\text{O}_3\text{-I}_2$ mixtures, with detection of IO radicals by time-resolved absorption spectroscopy at 427.2 nm. A cross-section of $(3.6 \pm 0.5) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ was used to determine k . The total pressure was 78 mbar N_2 . OIO product detected by absorption spectroscopy.
- 25 (e) Pulsed laser photolysis with detection of IO radicals by absorption spectroscopy using time-resolved charge-coupled detection (CCD) in the A-X system at 400 nm to 470 nm. The cross-section at 427.2 nm was measured to be $(1.9 \pm 0.17) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ (1.13 nm resolution). The differential cross section used to determine [IO] decreased by $\sim 45\%$ on increasing the temperature from 220 K to 335 K. The total pressure was 130 mbar to 1000 mbar of N_2 .

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(f) Discharge flow system with RF detection of I atoms after titration of IO radicals with NO. The total pressure was 2.5 mbar of He. Branching ratio k_2/k from analysis of I atom measurements in the absence of NO.

5 (g) Flash photolysis system with detection by absorption spectroscopy. The pressure dependence of the branching ratio to produce I atoms was based on the pressure dependence of k in the presence of excess O_3 .

(h) Based on I_2 formation at short reaction times, and on comparison of rate coefficients measured in the presence and absence of O_3 , with $k(\text{presence of } O_3)/k(\text{absence of } O_3)=0.73$ at 1 bar.

10 (i) Based on product absorptions due to I_2 , OIO and an unknown broad-band absorption at $\lambda \leq 400$ nm assigned to I_2O_2 . The value of $\sigma(\text{OIO})$ used was based on the branching ratio for the reaction $IO + BrO \rightarrow Br + OIO$ determined by Bedjanian et al. (1998).

Preferred Values

15 $k = 9.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 5.4 \times 10^{-11} \exp(180/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–320 K.

$k_1/k < 0.05$ at 298 K.

$k_3/k = 0.38$ at 298 K and 1 bar.

Reliability

20 $\Delta \log k = \pm 0.1$ at 298 K.

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

$\Delta (k_3/k) = \pm 0.1$ at 298 K and 1 bar.

The recently reported (Laszlo et al., 1995; Harwood et al., 1997; Atkinson et al., 1999; Ingham et al., 2000; Bloss et al., 2001; Vipond et al., 2002) values of k show good agreement for the overall rate coefficient at room temperature, which is higher than previously reported by Sander (1986), Jenkin and Cox (1985) and Barnes et al. (1991) (who used a discharge flow technique). When the different values of the absorption cross-sections are taken into account, there is excellent agreement in the values of $k/\sigma(427\text{ nm})$ obtained by Laszlo et al. (1995), Harwood et al. (1997), Bloss et al. (2001) and Ingham et al. (2000). Using a value of $\sigma(\text{IO})=3.6\times 10^{-17}\text{ cm}^2\text{ molecule}^{-1}$ at 427 nm from the IUPAC evaluation (see data sheet on IO photolysis), and the mean value of $k/\sigma(427\text{ nm})=2.75\times 10^6\text{ cm s}^{-1}$ from these studies, gives the preferred value at 298 K of $k=9.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. The results of Vipond et al. (2002) and Atkinson et al. (1999) are consistent with this value.

All studies agree that the overall rate coefficient in the absence of excess O_3 is independent of pressure over the range 1 mbar to 1000 mbar. The fraction of the IO+IO reaction leading to I atom production from studies at higher pressures (Harwood et al., 1997; Atkinson et al., 1999; Sander, 1986) appears to be ~20% to 30%, with $(k_2+0.5k_3)/k\sim 0.2\text{--}0.3$ consistent with the quantum yield for I_2 -photosensitized decomposition of O_3 (Jenkin et al., 1985). However, Jenkin and Cox (1985) and Sander (1986) observed a falloff in k with decreasing pressure in the presence of excess O_3 , i.e., when the I atom products are recycled to form IO, suggesting that the fractional I atom yield increases as pressure decreases. This is consistent with the higher branching ratio k_2/k reported by Vipond et al. (2002). Bloss et al. (2001) observed OIO formation with a branching ratio of k_3/k in the range 0.30 to 0.48, based on an OIO absorption cross-section of $\sigma(\text{OIO})=1.07\times 10^{-17}\text{ cm}^2\text{ molecule}^{-1}$ at 524 nm deduced from the OIO yield in the IO+BrO reaction (Bedjanian et al., 1998; Rowley et al., 2001).

All studies show that I_2 formation is minor, with $k_1/k<0.05$ (Sander, 1986; Laszlo et al., 1995; Harwood et al., 1997; Bloss et al., 2001). Most authors have assumed

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that I_2O_2 is the other major product formed, although evidence for I_2O_2 formation is not unequivocal. Both Sander (1986) and Bloss et al. (2001) report products which absorb in the UV near 300 nm but no direct identification of the absorbing species has been reported.

5 Temperature-dependent rate coefficients have been reported by Sander (1986), Harwood et al. (1997) and Bloss et al. (2001). The high value of $E/R = -(1020 \pm 200)$ K reported by Sander (1986) reflects the large temperature coefficient obtained for σ . When the much weaker changes in σ are used (see data sheet on IO photolysis), the temperature dependence of k disappears. On balance the results of Bloss et al. (2001),
10 which take into account the changes in the yield of IO radicals from the $O + CF_3I$ reaction used to calibrate the absorptions, are preferred. The temperature dependence of Bloss et al. (2001) is used and the pre-exponential factor, A , is adjusted to fit the preferred 298 K rate coefficient. The error reflects the possibility of a zero E/R .

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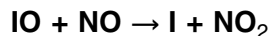
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$$\Delta H^\circ = -66 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.67 \pm 0.16) \times 10^{-11}$	298	Ray and Watson, 1981	DF-MS (a)
$(2.8 \pm 0.2) \times 10^{-11}$	298	Inoue et al., 1983	PLP-LIF (b)
$6.9 \times 10^{-12} \exp[(328 \pm 71)/T]$	242–359	Daykin and Wine, 1990	PLP-AS (c)
$(2.17 \pm 0.22) \times 10^{-11}$	298		
$1.02 \times 10^{-11} \exp[(185 \pm 70)/T]$	237–346	Turnipseed et al., 1995	PLP-LIF (d)
$(1.92 \pm 0.07) \times 10^{-11}$	298		
$(1.9 \pm 0.5) \times 10^{-11}$	295	Atkinson et al., 1999	PLP-AS (e)
$8.3 \times 10^{-12} \exp[(269 \pm 85)/T]$	273–353	Knight and Crowley, 2001	DF-MS (f)
$(2.17 \pm 0.20) \times 10^{-11}$	298		
$4.3 \times 10^{-12} \exp[(397 \pm 65)/T]$	233–346	Hölscher and Zellner, 2002	PLP-LIF (g)
$(1.68 \pm 0.11) \times 10^{-11}$	296		
$(1.82 \pm 0.10) \times 10^{-11}$	294	Dillon and Heard, 2003	PLP-LIF (h)
<i>Relative Rate Coefficients</i>			
$7.2 \times 10^{-12} \exp[(330 \pm 160)/T]$	293–366	Buben et al., 1996	DF-RF (i)
2.18×10^{-11}	298		

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- (a) IO radicals were produced by the reaction $I + O_3$ and monitored by MS in an excess of NO. Pressure varied between 1.33 and 2.8 mbar He.
- (b) IO formed from laser photolysis of $HI-N_2O$ at 193 nm, or $HI-O_3$ at 248 nm. Total pressure was 1.33 mbar He.
- (c) Pulsed laser photolysis of NO_2-I_2 mixtures at 351 nm. IO radical concentrations were monitored by longpath absorption spectroscopy in an excess of NO. k was found to be independent of pressure over the range 50 mbar to 260 mbar of N_2 .
- (d) Pulsed laser photolysis of N_2O-I_2 mixtures at 193 nm. IO radical concentrations were monitored by LIF in an excess of NO. k was found to be independent of pressure over the range 6.5 mbar to 130 mbar of N_2 .
- (e) Pulsed laser photolysis of $N_2O-CF_3I-NO-Ar$ mixtures at 193 nm. IO radicals were monitored by cavity ring-down spectroscopy at 445.04 nm. k was found to be independent of pressure over the range 12.5 mbar to 40 mbar of Ar.
- (f) IO radicals made by $O+I_2$ and detected by MS.
- (g) IO made by laser photolysis of N_2O-CF_3I at 193 nm. Pressure varied between 13 and 130 mbar synthetic air.
- (h) IO made by laser photolysis of N_2O-CF_3I at 193 nm. Pressure varied between 88 and 173 mbar N_2 or synthetic air.
- (i) IO made in photolysis of $CH_3I-O_2-O_3$ mixtures. Steady state I atom signals were monitored by resonance fluorescence and shown to depend on the relative concentration of O_3 and NO, and the relative rate coefficients for $I+O_3$ and $IO+NO$, i.e. $k/k(I+O_3)$ was derived. The expression for $k(T)$ was derived using the temperature dependent, recommended value for $k(I+O_3)$ (IUPAC, 2003).

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Preferred Values

$k = 1.95 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 7.15 \times 10^{-12} \exp(300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–370 K.

5 Reliability

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

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

Comments on Preferred Values

10 Most of the available rate coefficient data for this reaction (Ray and Watson, 1981; Inoue et al., 1983; Daykin and Wine, 1990; Turnipseed et al., 1995; Buben et al., 1996; Atkinson et al., 1999; Knight and Crowley, 2001; Hölscher and Zellner, 2002; Dillon and Heard, 2003) are in good agreement, only the result of Inoue et al. (1983) is anomalously high. The preferred value of $k = 1.95 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K is the mean of all other values.

15 The preferred expression for $k(T)$ is obtained by taking the mean of the values of E/R of Daykin and Wine (1990), Turnipseed et al. (1995), Knight and Crowley (2001), Hölscher and Zellner (2002) and Buben et al. (1996) and combining it with a pre-exponential factor adjusted to give the preferred value of k at 298 K.

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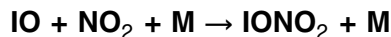
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$$\Delta H^\circ = -79 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.3 \pm 2.0) \times 10^{-31} [\text{N}_2]$	277	Jenkin and Cox, 1985	MM-A (a)
$7.7 \times 10^{-31} (T/300)^{-5.0} [\text{N}_2]$	254–354	Daykin and Wine, 1990	PLP-A (b)
$(3.6 \pm 1.0) \times 10^{-31} [\text{He}]$	298	Manguin et al., 1992	DF-MS (c)
$(7.9 \pm 2.2) \times 10^{-31} [\text{N}_2]$	298		
$(1.80 \pm 0.07) \times 10^{-31} (T/300)^{-2.6} [\text{O}_2]$	290–350	Larin et al., 1998	FR-F (d)
$4.1 \times 10^{-31} (T/298)^{-6.3} [\text{N}_2]$	238–298	Hölscher and Zellner, 2002	PLP-LIF (e)
$1.3 \times 10^{-30} (T/300)^{-4.5} [\text{N}_2]$	216–474	Allan and Plane, 2002	PLP-LIF (f)

Comments

(a) Photolysis of I_2 in the presence of O_3 producing IO radicals monitored by absorption at 427 nm in the presence of an excess of NO_2 . The total pressure was varied over the range 47–537 mbar of N_2 . The falloff curve was analyzed using $F_c=0.4$ by analogy to the $\text{BrO}+\text{NO}_2+\text{M}$ reaction. A small correction was made for a second-order component to the IO radical kinetics at higher pressures.

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(b) IO radicals generated by pulsed laser photolysis of I₂-NO₂-N₂ mixtures at 351 nm; IO radicals monitored by absorption at 427 nm. Pressure range 53–1000 mbar. The data were extrapolated to the low- and high-pressure rate coefficients using $F_c=0.4$.

5 (c) IO radicals and IONO₂ detected by MS. IO radicals were generated by the reaction O+I₂→IO+I. The pressure range was 1.6–2.8 mbar of He. Using a relative third-body efficiency of N₂ and He for the analogous BrO+NO₂+M (ratio $k_0(\text{N}_2)/k_0(\text{He})=2.2$) from Sander et al. (1981), the value reported above was derived.

10 (d) I atoms generated by photolysis of a flow of CH₃I at 254 nm; IO radicals formed by the reaction I+O₃→IO+O₂. Pressure range 1.3–8 mbar of O₂. Assuming a ratio of $\beta_c(\text{N}_2)/\beta_c(\text{O}_2)=1.4$, the expression $k_0=2.50\times 10^{-31} (T/300)^{-2.6} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290 K to 350 K was derived.

15 (e) Laser flash photolysis of mixtures of O₃, CF₃I and NO₂ in air with pulsed LIF detection of IO. Pressure range 50–400 mbar. Evaluation of the falloff curve with $F_c=0.6$. Rate coefficients about 20% below those from Daykin and Wine (1990).

20 (f) Laser flash photolysis of NO₂ in the presence of CF₃I and N₂ with LIF detection of IO. Falloff extrapolation with $F_c=0.57$ obtained from RRKM theory. Rate coefficients about 20% above data from Daykin and Wine (1990). Preliminary results by Blitz et al. (2000) are cited which are close to the present results.

Preferred Values

$k = 7.7 \times 10^{-31} (T/300)^{-5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–360 K.

Reliability

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

$\Delta n = \pm 2$.

Comments on Preferred Values

- 5 The preferred values for k_0 are an average of the data of Daykin and Wine (1990), the value of Maguin et al. (1992) derived with the given ratio of efficiencies for N_2 and He, the data from Hölscher and Zellner (2002), extrapolated with $F_c=0.4$ instead of 0.6, and the data from Allan and Plane (2002). The measurements of Larin et al. (1998) are a factor of 4 lower than the preferred values and need to be confirmed.

10 High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.6 \pm 0.6) \times 10^{-11}$	277	Jenkin and Cox, 1985	MM-A (a)
1.55×10^{-11}	254–354	Daykin and Wine, 1990	PLP-A (b)
1.0×10^{-11}	238–298	Hölscher and Zellner, 2002	PLP-LIF (c)
$6.5 \times 10^{-12} (T/300)^{-1.3}$	216–474	Allan and Plane, 2002	PLP-LIF (d)

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Comments

(a) See comment (a) for k_0 . The rate coefficient k_∞ was obtained from a fit of the falloff curve using $F_c=0.4$.

(b) See comment (b) for k_0 .

(c) See comment (e) for k_0 .

(d) See comment (f) for k_0 .

Preferred Values

$k_\infty = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–360 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 250–360 K.

Comments on Preferred Values

The preferred values for k_∞ are based on the data of Daykin and Wine (1990). Falloff extrapolations are made with $F_c=0.4$, independent of temperature over the range 250 to 360 K. If extrapolated with this F_c instead of $F_c \approx 0.6$, the measurements by Hölscher and Zellner (2002) and Allan and Plane (2002) are consistent with the preferred k_∞ .

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- Larin, I. K., Nevozhai, D. V., Sapasskii, A. I., and Trofimova, E. M.: Kinet. Catal., 39, 666, 1998.
- 10 Maguin, F., Laverdet, G., Le Bras, G., and Poulet, G.: J. Phys. Chem., 96, 1775, 1992.
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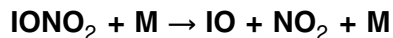
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III.A4.97



$$\Delta H^\circ = 79 \text{ kJ}\cdot\text{mol}^{-1}$$

Falloff range

5 No direct measurements are available.

Preferred Values

k (1 bar of air) = $1.1 \times 10^{15} \exp(-12060/T) \text{ s}^{-1}$ over the temperature range 240–305 K.

Reliability

10 $\Delta \log k = \pm 1$ at 300 K.

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

Comments on Preferred Values

15 The expression was obtained by Allan and Plane (2002) by inverting an RRKM fit of rate coefficient measurements of the reverse reaction. Measurements of IO profiles at 473 K and 300 Torr indicated the presence of IONO₂ dissociation which is consistent with the proposed rate expression.

References

Allan, B. J. and Plane, J. M. C.: J. Phys. Chem. A, 106, 8634, 2002.

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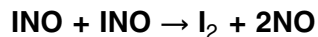
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III.A4.98



$$\Delta H^\circ = 0.3 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$8.4 \times 10^{-11} \exp(-2620/T)$	320–450	van den Bergh and Troe, 1976	PLP-UVA
1.3×10^{-14}	298*		
$2.9 \times 10^{-12} \exp(-1320/T)$	298–328	Basco and Hunt, 1978	FP-UVA
3.4×10^{-14}	298		

Preferred Values

$$k = 1.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 8.4 \times 10^{-11} \exp(-2620/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 300\text{--}450 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.4 \text{ at } 298 \text{ K.}$$

$$\Delta (E/R) = \pm 600 \text{ K.}$$

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Comments on Preferred Values

The results from the study of van den Bergh and Troe (1976) are preferred over those from Basco and Hunt (1978) because of a much wider range of conditions studied.

5 References

Basco, N. and Hunt, J. E.: *Int. J. Chem. Kinet.*, 10, 733, 1978.
van den Bergh, H. and Troe, J.: *J. Chem. Phys.*, 64, 736, 1976.

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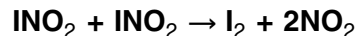
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$$\Delta H^\circ = 8.4 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

5

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
1.7×10^{-14}	350	van den Bergh and Troe, 1976	PLP-UVA
$4.7 \times 10^{-13} \exp(-1670 \pm 340/T)$	277.7–344.85	Gawler et al., 2003	FP-UVA

Preferred Values

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

$k = 4.7 \times 10^{-13} \exp(-1670/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–350 K.

10

Reliability

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

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

Comments on Preferred Values

15

The preferred values are based on the new measurements of Gawler et al. (2003). The measured rate constant at a single temperature of 350 K from van den Bergh and

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Troe (1976) is higher by a factor of 4, but uncertainties in both studies are large.

References

Gawler, K. S., Boakes, G., and Rowley, D. M.: Phys. Chem. Chem. Phys., 3632, 2003.
van den Bergh, H. and Troe, J.: Chem. Phys., 64, 736, 1976.

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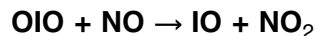
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III.A4.100



$$\Delta H^\circ = -17.9 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$7.6 \times 10^{-13} \exp[(607 \pm 128)/T]$	235-320	Plane et al., 2006	PLP-CRDS (a)
$(6.0 \pm 1.1) \times 10^{-12}$	298		

Comments

(a) OIO formed in self-reaction of IO, was produced by 193 nm photolysis of N_2O in the presence of CF_3I . The rate coefficient k was determined from the decay of OIO in the presence of excess NO. [OIO] measured by time resolved cavity ring-down spectroscopy (CRDS) at 567.808 nm. k was independent of pressure in the range 27–96 mbar at 300 K.

Preferred Values

$k = 6.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.1 \times 10^{-12} \exp(542/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–320 K.

Reliability

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

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

Comments on Preferred Values

5 The single experimental study provides well defined rate constants over the given pressure and temperature range, despite the complex source chemistry for the OIO radical. The observed rate constants and their temperature and pressure dependence were well reproduced by quantum chemical and RRKM calculations using a potential surface with a weakly bound OIONO intermediate which dissociates into IO+NO₂ products. Even at 1 bar pressure significant formation of OIONO is not predicted to occur. The authors recommend the expression: $(1.1 \pm 0.4) \times 10^{-12} \exp[(542 \pm 130)/T]$ for k (cm³ molecule⁻¹ s⁻¹) at 1 bar, taking account of experimental uncertainties and the theoretical analysis, which is adopted for the preferred value for formation of IO+NO₂ all pressures.

15 References

Plane, J. M. C., Joseph, D. M., Allan, B. J., Ashworth, S. H., and Francosco, J. S.: J. Phys. Chem. 110, 93, 2006.

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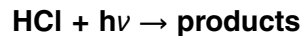
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Appendix 5: Photochemical Reactions

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Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HCl + $h\nu$ → H + Cl	432	277

Preferred Values

Absorption cross-sections for HCl at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
140	211	180	58.8
145	281	185	31.3
150	345	190	14.5
155	382	195	6.18
160	332	200	2.56
165	248	205	0.983
170	163	210	0.395
175	109	215	0.137
		220	0.048

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Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are those reported by Inn (1975). Photolysis is expected to occur with unit quantum efficiency.

References

- Inn, E. C. Y.: J. Atmos. Sci., 32, 2375, 1975.

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HOCl + $h\nu$ → products

Primary photochemical processes

Reaction			$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HOCl + $h\nu$	→ HO + Cl	(1)	239	500
	→ HCl + O(^3P)	(2)	432	277

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Preferred Values

Absorption cross-sections for HOCl at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	7.18	242	20.3	284	4.68
202	6.39	244	19.8	286	4.79
204	5.81	246	19.0	288	4.95
206	5.46	248	18.1	290	5.13
208	5.37	250	17.0	292	5.33
210	5.54	252	15.8	294	5.52
212	5.98	254	14.6	296	5.71
214	6.68	256	13.3	298	5.86
216	7.63	256	12.1	300	5.99
218	8.81	260	10.9	302	6.08
220	10.2	262	9.73	304	6.12
222	11.6	264	8.68	306	6.12
224	13.2	266	7.75	308	6.07
226	14.7	268	6.94	310	5.97

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λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
228	16.2	270	6.25	312	5.84
230	17.5	272	5.69	314	5.66
232	18.7	274	5.29	316	5.45
234	19.6	276	4.94	318	5.21
236	20.2	278	4.74	320	4.95
238	20.5	280	4.64	322	4.67
240	20.6	282	4.62	324	4.38
326	4.09	358	1.11	390	0.491
328	3.79	360	1.06	392	0.447
330	3.50	362	1.02	394	0.405
332	3.21	364	0.985	396	0.364
334	2.94	366	0.951	398	0.325
336	2.68	368	0.919	400	0.288
338	2.44	370	0.888	402	0.254
340	2.22	372	0.855	404	0.222
342	2.03	374	0.822	406	0.194
344	1.84	376	0.786	408	0.168
346	1.69	378	0.748	410	0.144
348	1.55	380	0.708	412	0.124
350	1.43	382	0.667	414	0.105
352	1.33	384	0.624	416	0.089
354	1.24	386	0.580	418	0.075
356	1.17	388	0.535	420	0.063

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Quantum yield for HOCl photolysis at 298 K

$$\Phi_1 = 1.0 \text{ for } \lambda > 200 \text{ nm}$$

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values calculated with the recent expression given by Barnes et al. (1998) based on their data from the laser induced fluorescence of HO and on the data of Burkholder (1993). In the Barnes (1998) study a weak absorption centered at 380 nm that extends down to 480 nm was observed. The recommended values agree very well with the values reported by Jungkamp et al. (1988) measured in a long-path UV absorption flow cell between 230 and 392 nm. Earlier results are discussed in IUPAC, 1989 and IUPAC, 1992 evaluations. Discrepancies between studies arise in correcting for spectral interference from Cl₂O and Cl₂. The preferred quantum yield values are based on the results of Molina et al. (1980), Butler and Phillips (1983), Schindler et al. (1987) and Vogt and Schindler (1992). An upper limit of $\Phi_2 < 0.02$ was determined by Butler and Phillips (1983) at 308 nm. Relative yields of HO ($^2\Pi_{3/2}$)/HO($^2\Pi_{1/2}$) were found to be 2.0 at 266 nm and 1.5 at 355 nm (Fujiwara and Ishiwata, 1998).

References

- Barnes, R. J., Sinha, A., and Michelsen, H. A.: J. Phys. Chem. A, 102, 8855, 1998.
Burkholder, J. B.: J. Geophys. Res., 98, 2963, 1993.
Butler, P. J. D. and Phillips, L. F.: J. Phys. Chem., 87, 183, 1983.
Fujiwara, H. and Ishiwata, T.: J. Phys. Chem. A, 102, 3856, 1998.
IUPAC: Supplement III, 1989 (see references in Introduction).
IUPAC: Supplement IV, 1992 (see references in Introduction).
Molina, M. J., Ishiwata, T., and Molina, L. T.: J. Phys. Chem., 84, 821, 1980.

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5 Schindler, R. N., Liesner, M., Schmidt, S., Kirchner, U., and Benter, T.: J. Photochem. Photobiol. A. Chem., 107, 9, 1987.

Vogt, R. and Schindler, R. N.: J. Photochem. Photobiol. A. Chem., 66, 133, 1992.

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$$\text{OCIO} + h\nu \rightarrow \text{products}$$

Primary photochemical processes

Reaction			$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
OCIO + $h\nu$	$\rightarrow \text{ClO} + \text{O}({}^3\text{P})$	(1)	255	470
	$\rightarrow \text{Cl} + \text{O}_2$	(2)	26	4540

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Preferred Values

Absorption cross-sections of OCIO at the band peaks at 204 K, 296 K and 378 K

λ/nm	$10^{20} \sigma/\text{cm}^2$ 204 K	$10^{20} \sigma/\text{cm}^2$ 296 K	$10^{20} \sigma/\text{cm}^2$ 378 K
475.53		13	
461.15	17	17	16
446.41	94	69	57
432.81	220	166	134
420.58	393	304	250
408.83	578	479	378
397.76	821	670	547
387.37	1046	844	698
377.44	1212	992	808
368.30	1365	1136	920
359.73	1454	1219	984
351.30	1531	1275	989

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λ/nm	$10^{20} \sigma/\text{cm}^2$ 204 K	$10^{20} \sigma/\text{cm}^2$ 296 K	$10^{20} \sigma/\text{cm}^2$ 378 K
343.44	1507	1230	938
336.08	1441	1139	864
329.22	1243	974	746
322.78	1009	791	628
317.21	771	618	516
311.53	542	435	390
305.99	393	312	291
300.87	256	219	216
296.42	190	160	167
291.77	138	114	130
287.80	105	86	105
283.51	89	72	90
279.647	73	60	79
275.74	59	46	
272.93	53	33	

Quantum yield for OCIO photolysis at 298 K

$\Phi_1 = 1.0$ over the wavelength range 270–480 nm.

$\Phi_2 < 0.04$ between 365 and 450 nm.

5 *Comments on Preferred Values*

The preferred values of the absorption cross-sections at the peak of the bands [a(0) to a(26)] at 204 K, 296 K, and 378 K are the values reported by Wahner et al. (1987). The bands become appreciably sharper with decreasing temperature (Wahner et al.,

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1987). However, the integrated band intensities remain constant for all bands between 204 K and 296 K, and, therefore, the solar photolysis rate is not expected to have a significant temperature dependence. Photoabsorption measurements of OCIO over the wavelength range of 125 to 470 nm at 298 K have been carried out by Hubinger and Nee (1994). Absorption cross-sections as a function of vibrational excitation are reported. The recommended quantum yield of unity for O-atom production is based on results reported by Colussi (1990), and results of earlier studies discussed by Watson (1977). Vaida and coworkers (1989, 1990) reported the detection of Cl atoms by resonance-enhanced multiphoton ionization (REMPI) in the photoisomerization of OCIO to ClOO followed by dissociation to Cl+O₂. Bishenden et al. (1991), using REMPI detection of Cl atoms, report that the quantum yield for Cl atom formation near 360 nm is 0.15±0.10. In contrast, Lawrence et al. (1990) using a technique involving charge transfer excitation of Cl-Xe collision pairs as a sensitive probe of Cl atoms, determined that the quantum yield for Cl atom production in the 359–368 nm region is 5×10^{-4}. In a molecular beam-photofragment study over the wavelength range 350–475 nm, Davis and Lee (1992) observed the dominant products to be ClO+O and also observed Cl atom yields reaching a maximum of 3.9% near 404 nm, decreasing to 0.2% in the wavelength range 350–370 nm, in qualitative agreement with the results of Lawrence et al. (1990). More recent experiments of Davis and Lee (1996) show that the quantum yield for Cl+O₂ production is 3.9±0.8% at 404 decreases at longer and shorter wavelengths and the branching ratio between the channels (1) and (2) depends on the OCIO excited state vibrational mode. Delmdahl et al. (1998) observed nascent Cl atom formation between 360 and 450 nm. A quantum yield less than 3.6% was determined between 365 and 450 nm. Below 365 nm Cl atom formation resulting from the photolysis of vibrationally excited ClO ($\nu \geq 4$) radicals was observed.

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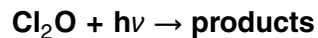
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Primary photochemical processes

Reaction			$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
Cl ₂ O + hν	→ Cl + ClO	(1)	142	840
	→ O + Cl ₂	(2)	168	710
	→ O + 2Cl	(3)	410	292

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Preferred Values

Absorption cross-sections of Cl₂O at 298 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	71.0	330	8.40
210	23.8	340	3.58
220	8.6	350	1.54
230	28.1	360	0.73
240	103	370	0.40
250	191	380	0.36
260	195	390	0.51
270	151	400	0.79
280	126	420	1.26
290	103	440	1.11
300	71.0	460	0.63
310	40.3	480	0.32
320	19.5	500	0.22

Comments on Preferred Values

5 The preferred values of the absorption cross-sections at 298 K are the values reported by Knauth et al. (1979). The preferred values are in excellent agreement with the values reported by Molina and Molina (1978), except for the 330–400 nm range where the values in Molina and Molina (1978) are higher, and they are in reasonable agreement with the values reported by Johnsson et al. (1995) ($\sigma=186 \times 10^{-20} \text{ cm}^2$ at 260 nm) and by Lin (1976) ($\sigma=183 \times 10^{-20} \text{ cm}^2$ at 260 nm). Values for the 150–200 nm wavelength region have been reported by Nee (1991).

10 Photolysis proceeds predominantly by breaking of the Cl-O bond to yield Cl+ClO.

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However, Sander and Friedl (1989) determined the quantum yield for formation of oxygen atoms from Cl_2O photolysis to be 0.25 ± 0.05 , the main products being $\text{Cl} + \text{ClO}$. In these experiments a broad-band photolysis source with a spectral distribution extending from the visible down to 180 nm was used, so that it was not possible to determine the wavelength dependence of the quantum yield. More recently, Nelson et al. (1994) have used photofragment translational energy spectroscopy in a molecular beam to study the photodecomposition of Cl_2O at 308, 248 and 193 nm. In all cases Reaction (1) occurs. At 308 nm the only channel is $\text{Cl} + \text{ClO}$; this is the major channel at 248 nm and a minor channel at 193 nm. At 248 nm the ClO fragment dissociates spontaneously. At 193 nm a concerted dissociation pathway leads to the formation of $\text{O} + \text{Cl}_2$. Almost all of the primary Cl_2O photoproducts dissociate. More recently, Nicolaisen et al. (1996) studied the pressure dependence of Cl_2O photodissociation. The observed pressure dependence of ClO formation was explained assuming that, after Cl_2O excitation at $\lambda > 300$ nm, a rapid intersystem crossing between two metastable states operates. These states were assumed to undergo competitive dissociation to $\text{Cl} + \text{ClO}$ and collisional relaxation to the ground state. However, this interpretation appears to be in disagreement with lifetime estimates by Moore et al. (1997). A detailed investigation of the dynamics of the complicated photodissociation process using the photoimaging technique was reported by Tanaka et al. (1998).

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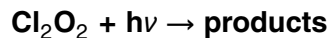
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Primary photochemical processes

Reaction			$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{Cl}_2\text{O}_2 + h\nu$	$\rightarrow \text{ClO} + \text{ClO}$	(1)	76	1580
	$\rightarrow \text{Cl} + \text{ClOO}$	(2)	91	1310

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Preferred Values

Absorption cross-sections of Cl₂O₂ at 200–250 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	384	250	609	300	72.2	350	8.2
202	353	252	580	302	65.8	352	7.9
204	325	254	545	304	59.9	354	6.8
206	299	256	505	306	54.1	356	6.1
208	275	258	632	308	79.0	358	5.8
210	251	260	422	310	43.3	360	5.5
212	232	262	381	312	38.5	362	4.5
214	217	264	345	314	34.6	364	4.1
216	208	266	312	316	30.7	366	3.8
218	206	268	283	418	28.0	368	3.5
220	212	270	258	320	25.6	370	3.2
222	227	272	237	322	23.4	372	2.9
224	249	274	218	324	21.4	374	2.7

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λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
226	280	276	202	326	19.2	376	2.4
228	320	278	186	328	17.8	378	2.2
230	365	280	173	330	716.7	380	2.1
232	415	282	160	332	15.6	382	1.9
234	468	284	147	334	14.4	384	1.7
236	518	286	136	336	13.3	386	1.6
238	563	288	125	338	13.1	388	1.4
240	600	290	115	340	12.1	390	1.3
242	626	292	105	342	11.5	392	1.2
244	639	294	95.4	344	10.9	394	1.1
246	643	296	87.1	346	10.1	396	1.0
248	632	298	79.0	348	9.0	398	0.9

Quantum yields for Cl_2O_2 photolysis

$\Phi_2 = 1.0$ throughout the range 200–398 nm.

Comments on Preferred Values

5 The preferred values of the absorption cross sections given here are the values recommended in the NASA (1997) evaluation. For the wavelength range 200–360 nm they are the smoothed average of the results reported by Cox and Hayman (1988), DeMore and Tschuikow-Roux (1990), Permien et al. (1988) and Burkholder et al. (1990); for wavelengths greater than 360 nm the values were derived from a linear extrapolation
 10 of $\log \sigma(\lambda)$ vs. λ using the expression: $\log(10^{20} \sigma/\text{cm}^2) = (7.589 - 0.01915\lambda)$. Huder and DeMore (1995) determined absorption cross-sections at 195 K over the range 200–450 nm. These values are significantly smaller than those given above, in some cases

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up to a factor of two. The differences could be due to the absorption of unwanted impurities, such as Cl_2O in the work of Huder and DeMore (1995). However, these absorption cross-sections should be confirmed by independent experiments. These studies indicate that, in the recombination reaction $\text{ClO} + \text{ClO} \rightarrow \text{products}$, the only stable species produced is ClOOCl . The structure of the recombination product has been established to be ClOOCl by the study of Birk et al. (1989) using submillimeter wave spectroscopy. Theoretical studies (McGrath et al., 1988, 1990; Jensen and Oddershede, 1990; Stanton et al., 1991, 1993) of thermochemical stabilities of Cl_2O_2 isomers are in agreement with these observations. The preferred quantum yield values are based on results of the study by Molina et al. (1990) in which the production of Cl atoms in the laser flash photolysis of ClOOCl at 308 nm was directly determined by time-resolved atomic resonance fluorescence. These results are in agreement with the interpretation of the steady-state photolysis experiments of Cox and Hayman (1988). More recently, laser flash photolysis/molecular beam experiments by Moore et al. (1999) performed at 248 and 308 nm give for the $\text{Cl} + \text{ClOO}$ channel a quantum yield of 0.9 ± 0.1 and for the complementary channel $\text{ClO} + \text{ClO}$ a value of 0.1 ± 0.1 . These results support the study of Molina et al. (1990).

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McGrath, M. P., Clemitshaw, K. C., Rowland, F. S., and Hehre, W. J.: J. Phys. Chem., 94, 6126, 1990.

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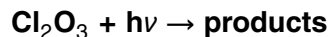
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Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{Cl}_2\text{O}_3 + h\nu \rightarrow \text{ClO} + \text{OCIO}$ (1)	44	2720
$\text{Cl}_2\text{O}_3 + h\nu \rightarrow \text{Cl} + \text{ClO}_3$ (2)	201	595

5 Preferred Values

Absorption cross-sections for Cl_2O_3 at 200–260 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
220	968	280	1136
225	930	285	890
230	908	290	642
235	883	295	435
240	904	300	288
245	989	305	176
250	1154	310	107
255	1352	315	56
260	1512	320	36
265	1594		
270	1544		
275	1376		

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The preferred values of the absorption cross-sections are those reported by Burkholder et al. (1993). They show no dependence on temperature over the range 200–260 K. The results of this more direct study of Burkholder et al. (1993) are preferred over those of Hayman and Cox (1989). These two studies (Hayman and Cox, 1989; Burkholder et al., 1993) are in agreement on the shape of the spectrum, but the values reported by Hayman and Cox (1989) are approximately 30–50% larger than those from Burkholder et al. (1993). A later flash photolysis study of Harwood et al. (1995) reports absorption cross-sections that below 310 nm are in between the values of Hayman and Cox (1989) and Burkholder et al. (1993), while at longer wavelengths the values are higher than the values of Hayman and Cox (1989) and Burkholder et al. (1993). The authors claim that no other UV-absorbing species than Cl₂O₃ were present in their experiments (Harwood et al., 1995). This problem needs further experimental investigation. The mechanism and quantum yield for photodissociation have not been determined.

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CINO + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CINO + $h\nu$ → Cl + NO	160	750

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Preferred Values

Absorption cross-sections for ClNO at 298 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	4320	246	45.2	302	10.3	370	11.0
192	5340	248	37.7	304	10.5	375	9.95
194	6150	250	31.7	306	10.8	380	8.86
196	6480	252	27.4	308	11.1	385	7.82
198	6310	254	23.7	310	11.5	390	6.86
200	5860	256	21.3	312	11.9	395	5.97
202	5250	258	19.0	314	12.2	400	5.13
204	4540	260	17.5	316	12.5	405	4.40
206	3840	262	16.5	318	13.0	410	3.83
208	3210	264	15.3	320	13.4	415	3.38
210	2630	266	14.4	322	13.6	420	2.89
212	2180	268	13.6	324	14.0	425	2.45
214	1760	270	12.9	326	14.3	430	2.21
216	1400	272	12.3	328	14.6	435	2.20

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λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
218	1110	274	11.8	330	14.7	440	2.20
220	896	276	11.3	332	14.9	445	2.07
222	707	278	10.7	334	15.1	450	1.87
224	552	280	10.6	336	15.3	455	1.79
226	436	282	10.2	338	15.3	460	1.95
228	339	284	9.99	340	15.2	465	2.25
230	266	286	9.84	342	15.3	470	2.50
232	212	288	9.71	344	15.1	475	2.61
234	164	290	9.64	346	15.1	480	2.53
236	128	292	9.63	348	14.9	485	2.33
238	101	294	9.69	350	14.5	490	2.07
240	82.5	296	9.71	355	13.6	495	1.78
242	67.2	298	9.89	360	12.9	500	1.50
244	55.1	300	10.0	365	12.0		

Quantum yields for ClNO photolysis at 298 K

$\Phi = 1.0$ over the entire wavelength range.

Comments on Preferred Values

5 The preferred values of the absorption cross sections at 298 K for the wavelength range 190–350 nm are the values reported by Tyndall et al. (1987) and for the longer wavelengths are the values reported by Roehl et al. (1992). Roehl et al. (1992) determined values over the wavelength range 350–650 nm and the temperature range 223–343 K. Earlier results are discussed in NASA (1997). The preferred quantum yield values are taken from Calvert and Pitts (1966). Relative yields of the spin-orbit states

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of $\text{Cl}(^2\Pi_{3/2})$ and $\text{Cl}(^2\Pi_{1/2})$ have been measured by Felder and Morley (1999) and Skorokhodov et al. (1996).

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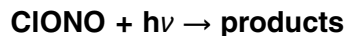
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Primary photochemical processes

Reaction			$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
ClONO + $h\nu$	$\rightarrow \text{Cl} + \text{NO}_2$	(1)	98	1220
	$\rightarrow \text{ClO} + \text{NO}$	(2)	136	880

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Preferred Values

Absorption cross-sections for ClONO at 231 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
235	215	320	80.3
240	176	325	75.4
245	137	330	58.7
250	106	335	57.7
255	65	340	43.7
260	64	345	35.7
265	69	350	26.9
270	90	355	22.9
275	110	360	16.1
280	132	365	11.3
285	144	370	9.0
290	144	375	6.9
295	142	380	4.1
300	129	385	3.3
305	114	390	2.2
310	105	395	1.5
315	98.1	400	0.6

Comments on Preferred Values

5 The preferred values of the absorption cross-sections at 231 K are the values reported by Molina and Molina (1977). Photolysis is expected to occur with unit quantum efficiency by breaking of the Cl-O bond to yield Cl+NO₂. The lifetime against photodissociation for ClONO in the atmosphere was calculated to be 2 to 3 min (Molina and

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Molina, 1977). Because of the instability of ClONO, Reaction (1) is the most probable photolysis pathway in the band centered around 290 nm.

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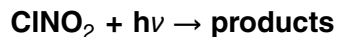
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Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{ClNO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_2$ (1)	142	840
$\text{ClNO}_2 + h\nu \rightarrow \text{ClNO} + \text{O}(^3\text{P})$ (2)	288	415

5 Preferred Values

Absorption cross-sections for ClNO_2 at 298 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	2690	290	17.3
200	468	300	14.9
210	320	310	12.1
220	339	320	8.87
230	226	330	5.84
240	133	340	3.54
250	90.6	350	2.04
260	61.3	360	1.15
270	35.3	370	0.69
280	22.0		

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Comments on Preferred Values

The preferred values of the absorption cross-sections are the values reported in the recent study of Ganske et al. (1992). They are in good agreement with the values reported by Illies and Takacs (1976/77) for 190–270 nm, the 270–370 nm values reported by Nelson and Johnston (1981), and the results by Hunter (1993). Nelson and Johnston (1981) determined that photolysis occurs with a quantum yield of unity (within experimental error) to produce Cl+NO₂ ($\Phi_1=0.93\pm 0.15$). They also reported a negligible production of oxygen atoms ($\Phi_2<0.02$). The product NO₂ from Reaction (1) is formed both in the electronic ground state and in an excited electronic state (Miller and Johnston, 1993; Carter et al., 1999).

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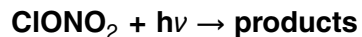
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Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
ClONO ₂ + hν	→ ClO + NO ₂ (1)	112	1065
	→ Cl + NO ₃ (2)	163	735
	→ ClONO + O(³ P) (3)	282	425

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Preferred Values

Absorption cross-sections for ClONO₂ at 296 and 220 K

λ/nm	$10^{20} \sigma/\text{cm}^2$ 296 K	$10^{20} \sigma/\text{cm}^2$ 220 K	λ/nm	$10^{20} \sigma/\text{cm}^2$ 296 K	$10^{20} \sigma/\text{cm}^2$ 220 K
200	282	270	315	1.14	
205	284		320	0.831	0.578
210	314	315	325	0.613	
215	342		330	0.466	0.329
220	332	335	335	0.367	
225	278		340	0.302	0.230
230	208	200	345	0.258	
235	148		350	0.229	0.186
240	105	96.7	355	0.208	
245	76.4		360	0.200	0.169
250	56.0	49.7	365	0.180	

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λ/nm	$10^{20} \sigma/\text{cm}^2$		λ/nm	$10^{20} \sigma/\text{cm}^2$	
	296 K	220 K		296 K	220 K
245	76.4		360	0.200	0.169
250	56.0	49.7	365	0.180	
255	43.2		370	0.159	0.136
260	33.8	29.1	375	0.141	
265	26.5		380	0.121	0.104
270	20.5	17.3	385	0.137	
275	15.7		390	0.091	0.077
280	11.9	9.83	395	0.076	
285	8.80		400	0.064	0.052
290	6.41	5.15	405	0.054	
295	4.38		410	0.044	0.034
300	3.13	2.40	415	0.036	
305	2.24		420	0.032	0.023
310	1.60	1.16	425	0.023	
			430	0.019	0.013

Quantum yields for ClONO₂ photolysis

$$\Phi_2(\lambda) = 0.4 + 4 \times 10^{-3} (\lambda/\text{nm} - 220).$$

$$\Phi_1(\lambda) = 1 - \Phi_2(\lambda).$$

$$\Phi_3 = 0.17 \text{ at } 220 \text{ nm.}$$

$$\Phi_3 < 0.10 \text{ at } 248 \text{ nm.}$$

$$\Phi_3 < 0.05 \text{ at } 308 \text{ nm.}$$

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The preferred values of the absorption cross-sections are taken from Burkholder et al. (1994) who measured values over the wavelength range 195–430 nm and the temperature range 220–296 K. They report (Burkholder et al., 1994) every 2 nm, values of σ at 296 K and values of the parameters A_1 and A_2 needed to compute the temperature dependence by the equation:

$$\sigma(\lambda, T)/\sigma(\lambda, 296) = 1 + A_1(T - 296) + A_2(T - 296)^2$$

In this data sheet, room temperature values at 5 nm intervals and values for 220 K at 10 nm intervals are given. These values are in good agreement with those reported in IUPAC (1992), which were based on the results of Molina and Molina (1979).

Preferred values for quantum yields are changed from those used (Chang et al., 1979; Margitan, 1983; Knauth and Schindler, 1983) for the recommendation in our previous IUPAC (1997) evaluation. A variety of experimental techniques such as atomic resonance fluorescence, tunable diode laser absorption and diode array spectroscopy have been employed by Ravishankara (1995) while photofragment translational spectroscopy was used by Moore et al. (1995) and Nelson et al. (1996). Broad band flash photolysis coupled with long-path UV-visible absorption spectroscopy in experiments by Nickolaisen et al. (1996), and laser flash photolysis coupled with resonance fluorescence in experiments by Tyndall et al. (1997) and by Goldfarb et al. (1997) and with visible absorption spectroscopy by Yokelson et al. (1997) extended the earlier work. The most recent studies (Ravishankara, 1995; Moore et al., 1995; Nelson et al., 1996; Nickolaisen et al., 1996; Tyndall et al., 1997; Goldfarb et al., 1997; Yokelson et al., 1997) approach a general agreement of the wavelength dependence of the quantum yields Φ_1 , Φ_2 , and Φ_3 , although some discrepancies, in particular pressure dependences, such as observed in Nickolaisen et al. (1996) were not reproduced in Tyndall et al. (1997), Goldfarb et al. (1997) and Yokelson et al. (1997), and remain unexplained. We here prefer the quantum yield results from Goldfarb et al. (1997) and Yokelson et al. (1997), which are consistent with the data from Ravishankara (1995), Moore et

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al. (1995), Nelson et al. (1996) and Tyndall et al. (1997). These results are $\Phi_1=0.60$, 0.40, and 0.35 for $\lambda=222$, 248, and 308 nm respectively, $\Phi_2=0.40$, 0.60, 0.65, and 0.93 for $\lambda=222$, 248, 308, and 352.5 nm, respectively, and $\Phi_3=0.17$, <0.10 , <0.05 for $\lambda=222$, 248, and 308 nm, respectively. A linear representation of $\Phi_2(\lambda)$ between 220
5 and 370 nm is given by $\Phi_2=0.4+4\times 10^{-3}(\lambda/\text{nm}-220)$.

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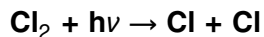
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Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{Cl}_2 + h\nu \rightarrow \text{Cl}({}^2\text{P}_{3/2}) + \text{Cl}({}^2\text{P}_{3/2})$	242	495

5 Preferred Values

Absorption cross-sections for Cl_2 at 298 K.

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
260	0.20	370	8.4
270	0.82	380	5.0
280	2.6	390	2.9
290	6.2	400	1.8
300	11.9	410	1.3
310	18.5	420	0.96
320	23.7	430	0.73
330	25.5	440	0.54
340	23.5	450	0.38
350	18.8	460	0.26
360	13.2	370	0.16

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The preferred values of the absorption cross-sections at 298 K are the values reported by Maric et al. (1993), which are in excellent agreement with those of Ganske et al. (1992). There is good agreement with earlier studies which are cited in IUPAC (1992). Maric et al. (1993) fitted the data for the wavelength region 250–550 nm with the following semi-empirical expression:

$$10^{20}\sigma = \alpha^{0.5} \times 27.3 \exp \left\{ -99.0 \alpha [\ln(329.5/\lambda)]^2 \right\} + \alpha^{0.5} \times 0.932 \exp \left\{ -91.5 \alpha [\ln(406.5/\lambda)]^2 \right\}$$

where $\alpha = \tanh(402.676/T)$

This expression combines the semi-empirical function originally proposed by Johnston et al. (1984) with the temperature dependence expressions proposed by Sulzer and Wieland (1952). The photodissociation occurs with a quantum yield of unity.

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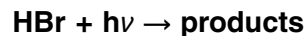
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Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{HBr} + h\nu \rightarrow \text{H} + \text{Br}$	366	327

5 Preferred Values

Absorption cross-sections of HBr at 298 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$
170	254
175	265
180	265
185	242
190	204
195	164
200	122
205	87.4
210	59.0
215	38.9
220	23.6
225	11.4
230	7.6

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Comments on Preferred Values

The preferred cross-section values are those determined by Huebert and Martin (1968) at temperatures near 298 K and measured with HBr pressures of 2.4–3.0 Torr. Previous measurements have been carried out by Goodeve and Taylor (1935) and Romand (1949). A primary quantum yield of unity was obtained with an N₂O actinometer (Martin and Willard, 1964). The branching ratio for photolysis forming Br(²P_{1/2}) and Br(²P_{3/2}) was determined in Regan et al. (1999).

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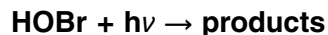
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Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HOBr + $h\nu$	$\rightarrow \text{HO} + \text{Br}$ (1)	207	578
	$\rightarrow \text{HBr} + \text{O}(^3\text{P})$ (2)	267	445
	$\rightarrow \text{BrO} + \text{H}$ (3)	394	304

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
260–545	Ingham et al., 1998	(a)

Quantum yield data

See Comments on Preferred Values.

Comments

- 10 (a) HOBr was generated by pulsed laser photolysis of flowing $\text{H}_2\text{O}_2\text{-Br}_2$ mixtures in an absorption cell through which the analysing beam could be passed twice to give an absorption path length of 2.6 m. Detection was achieved either by means of time-resolved photomultiplier measurements or by a diode array which could be

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gated from 0.06 ms to 5.06 ms. The spectral resolutions for the two techniques were 2 nm and 1.2 nm, respectively.

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Preferred Values

Absorption cross-sections of HOBr at 295 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
250	4.16	405	1.80
255	6.93	410	1.36
260	10.5	415	1.08
265	14.6	420	0.967
270	18.7	425	1.00
275	22.1	430	1.15
280	24.3	435	1.40
285	25.0	440	1.68
290	24.0	445	1.96
295	21.0	450	2.18
300	19.1	455	2.28
305	16.2	460	2.28
310	13.6	465	2.14
315	11.8	470	1.91
320	10.8	475	1.62
325	10.5	480	1.30
330	10.8	485	0.993
335	11.3	490	0.723
340	11.9	495	0.502
350	12.3	500	0.334
345	12.5	505	0.212
355	12.2	510	0.129

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λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
360	11.5	515	0.075
365	10.5	520	0.042
370	9.32	525	0.023
375	8.00	530	0.012
380	6.66	535	0.006
385	5.38	540	0.003
390	4.22	545	0.0001
395	3.24		
400	2.43		

Comments on Preferred Values

There remain significant uncertainties in the values of the absorption cross-sections despite a number of recent studies (Orlando and Burkholder, 1995; Benter et al., 1995; Deters et al., 1996; Rattigan et al., 1996; Ingham et al., 1998). However, the shape of the spectrum has been clarified. Orlando and Burkholder (1995), Benter et al. (1995) and Deters et al. (1996) observe two absorption bands between 200 and 400 nm with a rapid decline in the cross-sections beyond 400 nm. Rattigan et al. (1996) and Ingham et al. (1998) also observe these two bands but find another weak band with a maximum at ~ 460 nm as predicted by theoretical calculations (Francisco et al., 1996; Minaev et al., 1999). Further evidence for the long wavelength band comes from a laser photolysis study of Barnes et al. (1994) who observed HO production from HOBr photolysis over the range 400–600 nm. It now seems clear that the spectrum consists of three broad bands with maxima at ~ 284 nm, ~ 351 nm, and ~ 457 nm.

At the maximum of the short wavelength band the measured values of the cross-sections differ by $\sim 20\%$, whilst in the 350 nm region the differences become as much as a factor of three. It is likely that this scatter, and the difficulty in detecting the long wavelength band, are largely due to the presence of impurities such as Br_2O and Br_2 ,

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which absorb strongly in the same spectral region as HOBr.

In most of the studies (Orlando and Burkholder, 1995; Deters et al., 1996; Rattigan et al., 1996) HOBr was generated by reaction of Br₂O with H₂O, leading to the production of equilibrium mixtures of Br₂O, H₂O and HOBr. Benter et al. (1995) achieved smaller [Br₂O]/[HOBr] ratios by generation and elution of HOBr from aqueous solution and Ingham et al. (1998) attempted to circumvent the problems of impurities by in situ generation of the HOBr using pulsed laser photolysis of H₂O₂-Br₂ mixtures, calibrating the cross-sections relative to the better established cross-sections of Br₂. The study of Ingham et al. (1998) appears to have been the most successful in avoiding interference from impurities and their values are adopted as our preferred values. Their measurements (Ingham et al., 1998) only went down to 260 nm but they fitted their results to an expression consisting of the sum of three Gaussian terms and the range of our preferred values have been extended slightly using calculated values from this expression.

HO quantum yields close to unity have been observed for photolysis of HOI and HOCl, and a similar value would be expected for HOBr. The only experimental study is that of Benter et al. (1995) who obtained a value of >0.95 at 363 nm but this value is dependent on the cross-sections used. Confirmation of unit quantum yield is desirable.

Calculations of the atmospheric lifetime of HOBr by Ingham et al. (1998) using their own cross-sections give values of ~5 min in the lower stratosphere at a zenith angle of 40° and ~30 min at the surface at high zenith angles.

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BrO + h ν → products

Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
BrO + h ν	→ Br + O(³ P)	(1) 232	515
	→ Br + O(¹ D)	(2) 422	238

Absorption cross-section data

Wavelength range/nm	Reference	Comments
296–375	Cox et al., 1982	(a)
312–385	Wahner et al., 1988	(b)
338.5	Gilles et al., 1997	(c)

Quantum yield data

No experimental data are available.

Comments

- (a) BrO radicals were produced by square-wave modulated photolysis of Br₂-O₃ mixtures and detected in absorption at 0.22 nm resolution by molecular modulation

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spectroscopy using a multichannel analyser to collect the signal. The absolute cross-section at 338.3 nm was determined by measuring the kinetics of BrO production and removal.

5 (b) BrO radicals were generated in a flowing He carrier gas by reacting Br atoms with O₃ and passed into a 1 m long absorption cell coupled to a diode array spectrometer. Spectra were recorded at 298 K and 223 K with a resolution of 0.4 nm. Absolute cross-sections were determined at 338.5 nm at both temperatures by photolysis of Br-O₃ or Br-O₂ mixtures and monitoring the kinetics of the changes in [BrO].

10 (c) BrO radicals were produced by pulsed laser photolysis at 193 nm of N₂O-Br₂ mixtures in an absorption cell of 87 cm path length, and detected in time resolved experiments by means of a monochromator-photomultiplier combination. Pulsed photolysis of N₂O-O₂ mixtures, detecting O₃ production by absorption at 253.7 nm, was carried out in “back-to-back” experiments in the same system. The BrO absorption cross-sections were thus determined relative to the O₃ cross-section at 253.7 nm. The absorption cross-section at the peak of the (7,0) band was measured over the temperature range 204–388 K.

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Preferred Values

Absorption cross-sections of BrO at 303 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
300–305	200	340–345	515
305–310	259	345–350	399
310–315	454	350–355	228
315–320	391	355–360	172
320–325	600	360–365	161
325–330	753	365–370	92
330–335	628	370–375	51
335–340	589		

Comments on Preferred Values

5 The BrO radical has a banded absorption spectrum in the 290–380 nm range. The values of the absorption cross-sections at the band peaks are dependent on temperature and spectral resolution. The band locations, vibrational level assignments, and the values of the absorption cross-sections at several spectral resolutions, are reported in the paper by Wahner et al. (1988) which should be consulted for detailed information.

10 The strongest absorption feature is the (7,0) band at 338.5 nm for which the cross-section at 0.5 nm resolution was determined to be $(1.48 \pm 0.14) \times 10^{-17} \text{ cm}^2$ at 298 K. More recently a study by Gilles et al. (1997) from the same laboratory gives a value of $1.63 \times 10^{-17} \text{ cm}^2$. This latter value (Gilles et al., 1997) is preferred. In the same study, Gilles et al. (1997) investigated the temperature dependence of the absorption cross section at the peak of the 338.5 nm band over the range 204–388 K and found that it could be represented by the relationship $\sigma_{338}/10^{-17} \text{ cm}^2 = 3.29 - (5.58 \times 10^{-3}) T$.

15 The preferred values given in the Table are the values of the cross-section aver-

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aged over 5 nm intervals reported by Cox et al. (1982), which are in good agreement with those of Wahner et al. (1988) and Gilles et al. (1997). Cox et al. (1982) used their data to calculate a lifetime against solar photoexcitation of 30 s for a solar zenith angle of 30 degrees. Earlier studies are discussed in previous evaluations (CODATA, 1980, 1984) .

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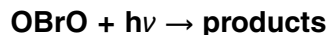
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Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
OBrO + $h\nu$	$\rightarrow \text{Br} + \text{O}_2$ (1)	-52	-
	$\rightarrow \text{BrO} + \text{O}(^3\text{P})$ (2)	205	584

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
400–600	Rattigan et al., 1994	(a)
385–645	Miller et al., 1997	(b)
390–630	Knight et al., 2000	(c)

Comments

(a) Bromine-sensitized photodecomposition of ozone at 380 nm to 480 nm. After subtraction of absorbances due to O_3 and Br_2 , the residual spectrum consisted of absorption bands from 400 nm to 600 nm superimposed on a continuum, with a maximum absorption near 505 nm. This spectrum was attributed to OBrO because of its strong resemblance to the OCIO absorption spectrum. Because absolute amounts of OBrO were not determined, absolute absorption cross-section values were not estimated. The spectral features show clear signs of broadening

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as T was increased from 273 K to 339 K, indicating temperature dependence of cross sections in the bands.

- 5 (b) Molecular bromine and products of an O_2 -He discharge flowed through an absorption cell at 250 K. Strong OBrO signals were observed after pumping on the condensate collected on the cell walls. An experimental and theoretical analysis of the $C(^2A_2) \leftarrow X(^2B_1)$ absorption spectrum from 385 nm to 645 nm is presented, and a complete set of transition energies and assignments is given. Because absolute amounts of OBrO were not determined, absolute absorption cross-section values were not derived.
- 10 (c) Products of a Br_2 - O_2 -He discharge flow were collected in a cold trap followed by evaporation at warmer temperatures. OBrO concentrations were determined by chemical titration with excess NO yielding $NO_2 + BrO$, with quantitative measurement of the NO_2 product by UV absorption. Quantitative values of absorption cross-sections are reported over the wavelength range 400 nm to 560 nm. During this study another UV absorber, assumed to be an unspecified bromine oxide Br_xO_y , was observed to originate from this OBrO source.
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Preferred Values

Absorption cross-sections of OBrO at 298 K.

n	(n,0,0) ← (0,0,0) λ/nm	$10^{17} \sigma/\text{cm}^2$	(n,1,0) ← (0,0,0) λ/nm	$10^{17} \sigma/\text{cm}^2$
0	630.4	–	622.0	–
1	606.1	–	598.4	–
2	583.8	–	576.8	–
3	563.4	1.08	556.8	1.35
4	544.4	1.45	538.5	1.74
5	527.1	1.64	521.6	1.91
6	510.7	1.77	505.5	1.96
7	495.5	1.72	490.7	1.76
8	481.2	1.67	476.9	1.51
9	468.2	1.44	464.1	1.26
10	455.8	1.21	452.2	0.96
11	444.4	1.02	440.8	0.72
12	433.7	0.79	430.4	0.49
13	423.5	0.57	420.6	0.31
14	414.1	0.40	411.0	0.22
15	405.1	0.26	402.3	0.13
16	396.4	–	394.0	–
17	388.3	–	–	–

Comments on Preferred Values

- 5 The preferred cross-section values are taken from the study of Knight et al. (2000). This is the only study in which the concentration of OBrO was quantitatively determined,

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thereby allowing the derivation of absolute absorption cross-section values. The uncertainty in these values is estimated to be $\pm 30\%$. The transition assignments are those reported by Miller et al. (1997). No quantum yield data are available. However, the threshold for photodissociation to yield $\text{BrO} + \text{O}(^3\text{P})$ lies well beyond the wavelength of maximum absorption in the $C(^2A_2) \leftarrow X(^2B_1)$ envelope. By analogy with OCIO efficient photodissociation via Reaction (2) is expected to occur at $\lambda < 550 \text{ nm}$. The possibility of dissociation via Reaction (1) at longer wavelengths cannot be ruled out, but its contribution is expected to be minor if the analogy with OCIO is used.

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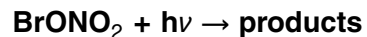
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Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
BrONO ₂ + hν	→ BrO + NO ₂	(1) 106	1129
	→ Br + NO ₃	(2) 139	861
	→ Br + NO + O ₂	(3) 155	772
	→ BrONO + O(³ P)	(4) 305	392
	→ Br + O(³ P) + NO ₂	(5) 347	345
	→ BrO + NO + O(³ P)	(6) 412	290
	→ BrONO + O(¹ D)	(7) 496	240

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–500	Burkholder et al., 1995	(a)
208–500	Deters et al., 1998	(b)

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Quantum yield data

Measurement	Wavelength /nm	Reference	Comments
$\Phi_2 = 0.28 \pm 0.09$	248	Harwood et al., 1998	(c)
$\Phi_2 = 1.01 \pm 0.35$	308		
$\Phi_2 = 0.92 \pm 0.43$	325.5		

Comments

- (a) Absorption spectra were measured at a resolution of ~ 0.5 nm in a 100 cm path length cell, thermostatted to ± 1 K. Relative cross-sections were obtained at 298, 250, and 220 K and placed on an absolute basis by determinations of the absolute cross-section at 330 nm at temperatures of 298 K, 273 K, 250 K, and 235 K. The concentrations of BrONO₂ were determined by pressure measurements and corrections were made to the absorption and concentration measurements for a number of impurities, particularly Br₂.
- (b) Spectra were recorded at 0.23–0.46 nm resolution using a flowing system with a multipass absorption cell of 270 cm optical path length coupled to a spectrograph and multichannel analyser. BrONO₂ concentrations were determined by photolysis of BrONO₂-Br₂ mixtures to completion, and measurement of the Br₂ concentrations by optical absorption at wavelengths > 500 nm. Absorption cross-sections for BrONO₂ were obtained at 298 K and 230 K.
- (c) Excimer laser photolysis at 248 nm, 308 nm, and 325.5 nm of flowing mixtures of BrONO₂ and N₂ or O₂. [NO₃] was monitored by time resolved diode laser absorption at 661.9 nm. The laser fluence was calibrated by N₂O₅ photolysis and BrONO₂ and N₂O₅ concentrations were determined by UV absorption. The measured quantum yields were pressure independent over the range 200–790 mbar.

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Preferred Values

Absorption cross-sections of BrONO₂ at 298 K and 230 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 230 K	λ/nm	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 230 K
200	680	553	355	6.52	6.62
205	520	447	360	5.99	6.07
210	361	345	365	5.43	5.51
215	292	294	370	4.89	4.94
220	256	265	375	4.35	4.40
225	230	241	380	3.85	3.84
230	205	215	385	3.37	3.34
235	175	182	390	2.97	2.91
240	140	143	395	2.59	2.52
245	106	106	400	2.28	2.21
250	79.7	77.2	405	2.01	1.96
255	60.0	57.0	410	1.81	1.76
260	47.1	44.0	415	1.65	1.63
265	38.9	36.1	420	1.50	1.51
270	33.8	31.3	425	1.38	1.43
275	30.5	28.3	430	1.29	1.36
280	27.9	26.2	435	1.20	1.29
285	25.6	24.3	440	1.11	1.20
290	23.2	22.5	445	1.03	1.12
295	20.8	20.6	450	0.928	1.01
300	18.6	18.8	455	0.831	0.893

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λ/nm	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 230 K	λ/nm	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 230 K
305	16.5	17.0	460	0.742	0.785
310	14.5	15.2	465	0.652	0.664
315	12.7	13.4	470	0.566	0.492
320	11.3	11.8	475	0.461	0.431
325	10.2	10.4	480	0.392	0.329
330	9.32	9.50	485	0.397	0.240
335	8.62	8.79	490	0.249	0.167
340	8.06	8.18	495	0.207	0.105
345	7.57	7.66	500	0.150	0.062
350	7.01	7.12			

Quantum Yields at 298 K.

λ/nm	ϕ_2
248	0.28
308	1.0
325.5	0.92

Comments on Preferred Values

Our previous recommendations (IUPAC, 1997) for the absorption cross sections were taken from the study of Spencer and Rowland (1978) which were limited to the wavelength range 186–390 nm. The more recent studies of Burkholder et al. (1995) and Deters et al. (1998) extend the range to 500 nm and cover the temperature range 220–298 K. At 298 K there is good agreement among the three studies; our preferred values are a mean of the values from Burkholder et al. (1995) and Deters et al. (1998).

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There is less good agreement between the studies of Burkholder et al. (1995) and Deters et al. (1998) on the temperature dependence of the absorption coefficients. At 230 K values of σ obtained in the two studies (Burkholder et al., 1995; Deters et al., 1998) agree in the range 200–300 nm but differ by up to 25% in the range 300–500 nm, and whereas Burkholder et al. (1995) find a small decrease in σ in going from 298 K to 230 K, over most of the wavelength range, Deters et al. (1998) find an increase. The preferred values at 230 K are a mean of the values from Burkholder et al. (1995) and Deters et al. (1998).

The only quantum yield measurements are those of Harwood et al. (1998) who determined the NO_3 quantum yield at 248, 308, and 325.5 nm, and also gave estimates of the Br and BrO quantum yields. Their values for the NO_3 quantum yields are adopted as our preferred values.

References

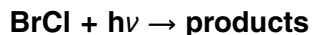
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IUPAC: Supplement V, 1997 (see references in Introduction).

Spencer, J. E. and Rowland, F. S.: J. Phys. Chem., 82, 7, 1978.



Primary photochemical transitions

Reaction	$\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
BrCl + $h\nu$ → Cl + Br	219	546
→ Cl($^2\text{P}_{1/2}$) + Br	229	521
→ Cl + Br($^2\text{P}_{1/2}$)	263	454

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–510	Seery and Britton, 1964	(a)
200–600	Maric et al., 1994	(b)
190–560	Hubinger and Nee, 1995	(c)

The two most recent spectra (see Comments b and c) may be conveniently compared in a data base coordinated by A. Nölle, (UV/VIS Spectra of Atmospheric Constituents, Version 1, 1999) and administered by DLR (Deutsches Zentrum für Luft-und Raumfahrt e.V., ATMOS User Center DFD-AUC, <http://auc.dfd.dlr.de/>).

Comments

(a) The authors used the same apparatus for the BrCl absorption cross sections at three different Cl₂/Br₂ mixing ratios as for the measurements of both the Cl₂

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and Br_2 cross sections and an equilibrium constant $K_{\text{BrCl}}=8.1$ for the equilibrium $\text{Cl}_2+\text{Br}_2\leftrightarrow 2\text{BrCl}$ (Evans et al., 1955). The resulting cross sections are slightly higher than the recommended value.

(b) The equilibrium constant K_{BrCl} as well as the absorption spectrum of BrCl have been measured using twelve different Cl_2/Br_2 mixing ratios in nine overlapping spectral ranges of about 70 nm spectral width resulting in a spectral resolution of 0.2 nm. At least ten independent spectra were recorded at different total pressures (Cl_2 , Br_2 and BrCl). The interference from a pressure-dependent component of the Br_2 vapor was negligible under the chosen experimental conditions. The value of K_{BrCl} was iteratively adjusted until minimum deviation occurred between the observed and calculated absorption spectrum of BrCl in all the regions of overlap: $K_{\text{BrCl}}=10.1\pm 1.1$ at 298 K leads to a third law value of $\Delta H_f^\circ=14.31$ kJ/mol.

(c) Mixtures of Cl_2 and Br_2 in 670 mbar of Ar were prepared in an evacuable gas flow line. The equilibrium concentrations have been obtained using $K_{\text{BrCl}}=6.4$ (Matrrow et al., 1954). The low pressures used in the present study (0.2 to 12.0 mbar) minimized the interference of Br_2 dimers. The limit to the red at $\lambda>500$ nm is given by instrument noise. Graphical comparison between the measured spectrum and the results from the literature (Seery and Britton, 1964; Maric et al., 1994) shows only minor differences. The BrCl spectrum was deconvoluted using a semi-logarithmic gaussian distribution function into four components with maxima at 228.33 (UV band), 376.39 ($C^1\Pi_1$), 454.92 ($B^3\Pi_0^+$) and 533.05 nm ($A^3\Pi_1$).

No Quantum Yield Data available.

Absorption cross-sections of BrCl at 298 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	2.95	410	22.39
210	4.27	420	17.78
220	6.31	430	14.45
230	6.61	440	12.59
240	5.62	450	10.72
250	4.07	460	9.33
260	5.50	470	7.94
270	1.29	480	6.31
280	0.66	490	5.01
290	0.39	500	3.39
300	0.56	510	2.63
310	1.51	520	1.66
320	4.07	530	1.10
330	9.12	540	0.66
340	17.00	550	0.41
350	28.18	560	0.25
360	34.67	570	0.144
370	41.69	580	0.832
380	39.81	590	0.0479
390	33.88	600	0.0251
400	28.18		

Comments on Preferred Values

The data of Maric et al. (1994) are recommended because it is the most comprehensive data set to date available which is internally consistent using an equilibrium

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constant $K_{\text{BrCl}}=10.1\pm 1.1$ at 298 K which is measured in the same study. The absorption cross sections of BrCl agree in the regions of overlap between the spectral fragments to better than $\pm 2\%$, and it is estimated that the accuracy is better than $\pm 3\%$ in the range $\lambda=200\text{--}550$ nm. In the range 550–600 nm the agreement between spectral fragments is better than $\pm 15\%$ for an overall accuracy in this range of better than $\pm 20\%$. Spectral deconvolution in terms of three contributing bands with maxima at 227.6, 372.5 and 442.4 nm has been obtained. Combining the values of σ_{BrCl} with the results of Sulzer and Wieland (1952) obtains the temperature and wavelength dependence of the UV/Vis absorption spectrum of BrCl. A quantum yield of unity for the dissociation of BrCl is expected.

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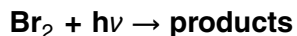
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Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{Br}_2 + h\nu \rightarrow \text{Br}(^2\text{P}_{3/2}) + \text{Br}(^2\text{P}_{3/2})$	193	620
$\text{Br}_2 + h\nu \rightarrow \text{Br}(^2\text{P}_{3/2}) + \text{Br}(^2\text{P}_{1/2})$	237	505

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–750	Passchier et al., 1967	(a)
220–290	Wen and Noyes, 1972	(b)

Quantum yield data

See Comments on Preferred Values.

Comments

- 10 (a) Spectra were obtained using a Beckman DU spectrophotometer equipped with a thermostatted optical cell. Br_2 concentrations were determined by pressure measurement or by titration with $\text{Na}_2\text{S}_2\text{O}_3$. Values of the absorption cross-section are given for temperatures of 298 K, 348 K, 423 K, 498 K, 573 K, 648 K, and 613 K.

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In the wavelength range 200–240 nm the measured cross sections are pressure dependent, attributed to Br₄ formation. From the pressure dependences, values of the absorption cross sections for Br₄ and Br₂ were derived in the range 200–230 nm.

- 5 (b) Spectra were obtained with a Beckman DU spectrophotometer equipped with a cell of optical path length 9.8 cm and thermostatted to 303 K. Br₂ concentrations were derived by pressure measurements. Deviations from Beer's Law which were observed, and attributed to Br₄ formation, were used to study the equilibrium between Br₂ and Br₄ and to derive values of $\sigma(\text{Br}_2)$ corrected for Br₄ absorption.

Preferred Values

Absorption cross-sections of Br₂ at 298 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	0.562	350	3.48
205	0.723	355	5.63
210	0.870	360	8.65
215	0.983	365	12.7
220	1.04	370	17.8
225	1.06	375	23.9
230	1.01	380	30.7
235	0.925	385	37.9
240	0.808	390	45.1
245	0.676	395	51.8
250	0.543	400	57.4
255	0.422	405	61.6
260	0.316	410	64.2

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λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
265	0.229	415	65.1
270	0.161	420	67.7
275	0.180	425	60.8
280	0.0728	430	60.1
285	0.0471	435	57.1
290	0.02398	440	54.0
295	0.0188	445	51.2
300	0.0124	450	48.7
305	0.0101	455	46.7
310	0.0135	460	45.1
315	0.0274	465	43.8
320	0.0626	470	42.8
325	0.141	475	41.7
330	0.299	480	40.3
335	0.602	485	38.6
340	1.14	490	36.6
345	2.05	495	34.3
		500	31.8

Quantum yields

See Comments on Preferred Values.

Comments on Preferred Values

- 5 Maric et al. (1994) have evaluated the available absorption cross section data for Br_2 and have fitted the most reliable data to an expression giving σ over the range

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200–600 nm as the sum of four terms each representing the contribution to σ of one of the separate overlapping absorption bands of the spectrum. The data sets selected by Maric et al. (1994) were those of Passchier et al. (1967) and of Wen and Noyes (1972), which cover the whole wavelength range, are in excellent agreement and make due allowance for the deviations from Beer's Law which are observed in the 200–300 nm region, attributed to Br₄ formation. The findings of Maric et al. (1994) are accepted and our preferred values for the absorption cross-section at 298 K are calculated from the expression which they derived. They have also derived an extension of their expression for use at other temperatures.

In a more recent study covering the range 190–600 nm, Hubinger and Nee (1995) have obtained values of σ in excellent agreement with the expression of Maric et al. (1994) except in the 270–330 nm region where absorption cross-sections are small and only upper limits could be given.

At wavelengths longer than ~510 nm the spectrum consists of a banded region overlapping a continuum. High resolution spectroscopic studies (Zaraga et al., 1976; Hemenway et al., 1979) indicate rather smaller values for the contribution of the continuum absorption at long wavelengths than predicted by the expression of Maric et al. (1994).

Absorption of radiation in the range 200–510 nm is expected to lead to bond rupture with unit quantum efficiency, giving two ground state Br atoms or Br(²P_{3/2}) + Br(²P_{1/2}), as confirmed by photofragment spectroscopic studies (Busch et al., 1969; Lindeman and Wiesenfeld, 1979). There are no direct measurements of the quantum yield but in a study of the photoinitiated bromination of ethene Kistiakowsky and Sternberg (1953) showed that the quantum yield of Br production is approximately independent of wavelength in the range 480–680 nm.

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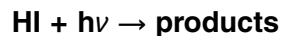
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Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{HI} + h\nu \rightarrow \text{H} + \text{I}$	298	401

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Preferred Values

Absorption cross-sections for HI at 298 K

λ/nm	$10^{19} \sigma/\text{cm}^2$	λ/nm	$10^{19} \sigma/\text{cm}^2$
190	4.8	255	4.0
195	5.7	260	3.2
200	6.5	265	2.4
205	7.3	270	1.8
210	7.9	275	1.3
215	8.2	280	0.93
220	8.4	285	0.63
225	8.3	290	0.42
230	7.9	295	0.27
235	7.3	300	0.17
240	6.6		
245	5.8		
250	4.9		

5 *Comments on Preferred Values*

HI has a continuous absorption spectrum with an onset at about 327 nm. Earlier measurements of absorption cross-sections were reported by Goodeve and Taylor (1935) and Romand (1949). The preferred values are based on more recent measurements of Huebert and Martin (1968) between 180 and 300 nm and Ogilvie (1971) between 192 and 313 nm. The preferred values were represented by the expression

$$\sigma = 8.39 \times 10^{-19} \exp[-(\lambda - 220.29)^2/1621.29]$$

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where λ is in units of nm and σ is in units of cm^2 .

Which fits very well the data of Huebert and Martin (1968) and Ogilvie (1971) over the wavelength range 190–300 nm in good agreement with determinations by Campuzano-Jost and Crowley (1999). The primary photochemical process forms H and I atoms with a quantum yield of about unity at 185 and 254 nm (Martin and Williard, 1964). The branching ratio for production of $\text{I}(^2\text{P}_{1/2})$ and $\text{I}(^2\text{P}_{3/2})$ was measured in Langford et al. (1998) as a function of the wavelength between 190 and 305 nm.

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HOI + $h\nu$ → products

Primary photochemical processes

Reaction			$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HOI + $h\nu$	→ HO + I	(1)	216	554
	→ HI + O(³ P)	(2)	345	347
	→ IO + H	(3)	404	296
	→ HI + O(¹ D)	(4)	535	224

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
280–500	Bauer et al., 1998	(a)
278–494	Rowley et al., 1999	(b)

Comments

(a) Laser photolysis of H₂O at 248 nm was used to produce HO radicals in the presence of I₂, and hence to produce HOI in situ. Absorptions were measured by a gated diode array, and at selected wavelengths by a photomultiplier. The HOI concentration was determined from the instantaneous I₂ loss. The spectrum consists of two unstructured bands at 340.4 nm [$\sigma_{\text{max}}=(3.85\pm 0.4)\times 10^{-19}\text{ cm}^2\text{ molecule}^{-1}$] and 406.4 nm [$\sigma_{\text{max}}=(3.30\pm 0.3)\times 10^{-19}\text{ cm}^2\text{ molecule}^{-1}$].

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(b) Same technique as in comment (a). Some irreproducibility in the 406 nm band was tentatively attributed to I₂O formation. Cross sections of $\sigma_{\max}=3.99 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ at 338.4 nm and $\sigma_{\max}=2.85 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ at 404.8 nm were obtained.

5 Quantum yield data

Quantum yield	Wavelength/nm	Reference	Comments
$\phi(1) = 1.05 \pm 0.13$	355	Bauer et al., 1998	(a)

(a) HOI was produced by pulsed laser photolysis of HNO₃ at 248 nm to produce HO radicals in the presence of I₂. A second 355 nm laser pulse interrogated the HOI produced and the photofragment product HO was observed by resonance fluorescence. Fresh reactants were introduced at each laser pulse. The quantity $\{\sigma^{\text{HOI}} \phi(\text{HO})^{\text{HOI}}\}$ at 355 nm was determined which, with the measured value of σ (see above), gave the cited value of ϕ .

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Preferred Values

Absorption cross-sections of HOI at 295 K

λ/nm	$10^{19} \sigma/\text{cm}^2$	λ/nm	$10^{19} \sigma/\text{cm}^2$
280	0.0077	390	2.66
285	0.0226	395	2.98
290	0.0589	400	3.22
295	0.137	405	3.32
300	0.286	410	3.27
305	0.541	415	3.07
310	0.926	420	2.75
315	1.45	425	2.35
320	2.07	430	1.92
325	2.72	435	1.50
330	3.29	440	1.13
335	3.70	445	0.813
340	3.85	450	0.563
345	3.77	455	0.376
350	3.47	460	0.242
355	3.04	465	0.150
360	2.58	470	0.0904
365	2.21	475	0.0525
370	1.98	480	0.0296
375	1.94	485	0.0161
380	2.07	490	0.0086
385	2.33		

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Quantum Yields

$\phi(1) = 1.0$ in the wavelength range 280–490 nm.

Comments on Preferred Values

- 5 The recommended values for the cross-sections are those given by Bauer et al. (1998). The data of Rowley et al. (1999) are in good agreement with the exception of some systematically higher values in the 405 nm band.

References

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IO + h ν \rightarrow products

Primary photochemical processes

Reaction			$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
IO + h ν	\rightarrow I + O(^3P)	(1)	240	500
	\rightarrow I + O(^1D)	(2)	430	280

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
427.2	Sander, 1986	(a)
340–450	Laszlo et al., 1995	(b)
340–480	Harwood et al., 1997	(c)
345–465	Atkinson et al., 1999	(e)
345–465	Bloss et al., 2001	(d)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 > 0.09 \pm_{0.26}^{0.19}$	355	Ingham et al., 2000	(f)

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- (a) Flash photolysis-absorption spectroscopy study. Cross-sections at the head of the 4-0 band at 427.2 nm were measured at six temperatures in the range 250 K to 373 K. A strong temperature dependence was observed at temperatures <315 K, with σ increasing with decreasing temperature.
- (b) Pulsed laser photolysis-absorption spectroscopy study. A cross-section of $\sigma(427.2 \text{ nm}) = (2.8 \pm 0.5) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 298 K was obtained, at a resolution of 0.3 nm.
- (c) Pulsed laser photolysis-absorption spectroscopy study. Cross-sections of $\sigma(427.2 \text{ nm}) = (3.0 \pm 0.4) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ and $(3.6 \pm 0.5) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ were reported for resolutions of 0.44 nm and 0.14 nm, respectively, at 298 K.
- (d) Pulsed laser photolysis of $\text{N}_2\text{O-CF}_3\text{I}$ mixtures. IO radicals were detected by time-resolved CCD measurements of the post-laser pulse mixtures in the range 340 nm to 470 nm. Cross-sections of $\sigma(427.2 \text{ nm}) = (1.9 \pm 0.2) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ (resolution of 1.13 nm) and $\sigma(395.5 \text{ nm}) = (5.7 \pm 0.5) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ were reported. They also reported a small temperature dependence of the cross-section at 427.2 nm, based on an analysis of the differential cross-section and taking into account the temperature and pressure dependence of the yield of IO radicals from the $\text{O}(^3\text{P}) + \text{CF}_3\text{I}$ reaction.
- (e) Pulsed laser photolysis of $\text{N}_2\text{O-CF}_3\text{I}$ mixtures. IO radicals were detected by time-resolved cavity ring-down spectroscopy (CRDS) at 445.40 nm (band head of rotationally resolved 2-0 band) and 455 nm (maximum of the diffuse 1-0 band). Cross-sections of $\sigma(445.40 \text{ nm}) = (7.3 \pm 0.7) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ and $\sigma(455 \text{ nm}) = (7.3 \pm 0.8) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ were obtained using absolute value of $1.05 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 298 K obtained by Laszlo et al. (1995) for the 2-0 band head at a resolution of 0.3 nm.

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(f) Pulsed laser photolysis (248 nm) of O₃-I₂ mixtures, with photolysis of IO radicals by second laser pulse at 355 nm after a fixed time delay. O(³P_j) detected by time-resolved RF. Quantum yield measured relative to NO₂ photolysis at the same wavelength.

5 Preferred Values

Absorption cross-sections for IO at 298 K.

λ/nm	$10^{18} \sigma/\text{cm}^2$	λ/nm	$10^{18} \sigma/\text{cm}^2$
345	0.78	410	7.53
350	1.00	415	5.18
355	1.36	420	9.04
360	1.85	425	4.17
365	2.25	430	6.11
370	2.99	435	6.92
375	3.57	440	1.61
380	4.42	445	4.94
385	4.63	450	1.02
390	5.65	455	2.36
395	6.55	460	0.90
400	6.407	465	0.39
405	7.09		

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Quantum Yields

$\phi(1) = 1.0$ throughout the wavelength range 345–465 nm.

Comments on Preferred Values

5 *Absorption Cross-Sections.* The measurements of the cross-sections at the band head of the 4-0 band at 427.2 nm by Laszlo et al. (1995), Harwood et al. (1997), Bloss et al. (2001) are in fairly good agreement when the effects of resolution are taken into account. These data (Laszlo et al., 1995; Harwood et al., 1997; Atkinson et al., 1999) suggest a slightly higher value than the earlier data of Sander
10 (1986), Stickel et al. (1988) and Cox and Coker (1983). We recommend a value of $\sigma(427.2 \text{ nm}) = (3.6 \pm 0.3) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ based on the measurements of Harwood et al. (1997) for the 4-0 band at high resolution (0.14 nm). The information from the studies of Harwood et al. (1997) and also of Atkinson et al. (1999) at 298 K on the IO band shape and cross section at high resolution can be used to calculate the
15 expected intensity and shape of the bands at lower resolution, which shows that the recent studies are consistent with this recommendation.

The study of Laszlo et al. (1995) showed that the vibronic band structure is superimposed on a broad continuous absorption which maximizes at ~ 400 nm. Other recent studies (Harwood et al., 1997; Bloss et al., 2001) confirm the presence of the underlying continuum, which makes a significant contribution to atmospheric photolysis. Bloss
20 et al. (2001) showed that IO absorption measurements in the 340 nm to 450 nm region can be influenced by the presence of an underlying absorption due to a product of the IO+IO reaction, and this was accounted for in their reported values for σ in the continuum region (Bloss et al., 2001). However Harwood et al. (1997) observed the same
25 decay kinetics when IO was monitored in the continuum region at 390 nm suggesting no interference due to product absorption. The agreement is good in the reported overall shape of the IO absorption envelope in the continuum between 350–400 nm where

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resolution is unimportant, from the three studies. The absolute cross sections reported by Bloss et al. (2001) in the continuum at 390 nm are a factor of 0.67 lower than those from Laszlo et al. (1995) and Harwood et al. (1997). The preferred values for the IO cross-sections averaged over 5 nm intervals in the 345 nm to 465 nm are the values given by Bloss et al. (2001), scaled upwards by a factor of 1.5 to compensate for the lower resolution-independent value of $\sigma(390 \text{ nm})$, obtained in this study.

The temperature dependence of $\sigma(427.2 \text{ nm})$ has been investigated by Sander (1986), Harwood et al. (1997) and Bloss et al. (2001). The studies of Harwood et al. (1997) and Bloss et al. (2001) did not reproduce the large increase in σ with decreasing temperature below 315 K observed by Sander (1986) although values of σ above 315 K are in good agreement (Sander, 1986; Harwood et al., 1997; Bloss et al., 2001). Bloss et al. (2001) found that the yield of IO from the $\text{O}(^3\text{P})+\text{CF}_3\text{I}$ reaction is apparently pressure and temperature dependent, and this was accounted for in deriving their expression for the small temperature dependence of $\sigma(427.2 \text{ nm})$. Harwood et al. (1997) assumed a constant yield of IO from the $\text{O}(^3\text{P})+\text{CF}_3\text{I}$ reaction which resulted in a temperature-independent cross-section σ at 427.2 nm. Since the temperature dependence is clearly quite small, cross-sections in the banded region at low resolution can be assumed to be temperature independent. Cross sections in the continuum region are assumed to be temperature and resolution independent.

Quantum Yields. Turnipseed et al. (1995) observed LIF from the (0,0), (2,0), (3,0) and (2,1) bands of the $\text{A}^2\Pi_{3/2}\leftarrow\text{X}^2\Pi_{3/2}$ transition of IO. The spectra are predissociated and the dissociation lifetime is $<10 \text{ ns}$ (Inoue et al., 1983). The lifetime of the upper state of IO formed in the A-X transition is thus so short that quenching, fluorescence and processes other than dissociation by Reaction (1) must be negligible, and therefore the predominant fate of IO following light absorption is dissociation to O+I. The measurement of Ingham et al. (2000) in the continuum at 355 nm confirms this conclusion for that region.

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OIO + h ν \rightarrow products

Primary photochemical processes

Reaction			$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
OIO + h ν	\rightarrow I + O ₂	(1)	30	3987
	\rightarrow IO + O(³ P)	(2)	288	415

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
465–667	Himmelmann et al., 1996	(a)
549.1	Spietz et al., 1998	(b)
548.6	Cox et al., 1999	(c)
548.6	Ingham et al., 2000	(d)
540–605	Ashworth et al., 2002	(e)

Quantum yield data ($\Phi = \Phi_1 + \Phi_1$)

Measurement	Wavelength/nm	Reference	Comments
$\Phi_1 < 0.15$ $\Phi_2 < 0.007$	532	Ingham et al., 2000	(f)

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- (a) Flash photolysis of a mixture of I_2 in O_3 with time-resolved UV-visible absorption spectroscopy. In addition to IO bands between $21\,500\text{ cm}^{-1}$ and $26\,000\text{ cm}^{-1}$ (385 nm to 465 nm), a new absorption spectrum between $15\,000\text{ cm}^{-1}$ and $21\,500\text{ cm}^{-1}$ (465 nm to 667 nm) was observed, which was attributed to the OIO radical by comparison of the derived spectroscopic constants with the known values for OCIO and OBrO.
- (b) Same technique as in comment (a). Fits to a complex mechanism yielded an estimate for $\sigma(\text{OIO})=(3.5\pm 1.5)\times 10^{-17}\text{ cm}^2\text{ molecule}^{-1}$ at 549.1 nm.
- (c) Pulsed laser photolysis of $N_2O\text{--}Br_2\text{--}CF_3I$ mixtures at 193 nm with time-resolved UV-visible absorption spectroscopy using a charged-coupled-device detection system. The branching ratio for OIO formation in the IO self-reaction was determined to be 0.38 ± 0.08 . This is based on an analysis assuming a branching ratio for OIO formation in the IO+BrO reaction of 0.8, as reported by Bedjanian et al. (1998) from a DF study in which the co-product Br was measured. A corresponding absolute value of $\sigma(\text{OIO})=(1.09\pm 0.21)\times 10^{-17}\text{ cm}^2\text{ molecule}^{-1}$ at 548.6 nm was derived. Absorption bands were observed from 495 nm to 600 nm.
- (d) Pulsed laser photolysis of a mixture of O_3 in I_2 with UV-visible absorption spectroscopy and resonance fluorescence detection. A conservative minimum OIO cross section of $2.7\times 10^{-17}\text{ cm}^2\text{ molecule}^{-1}$ at 548.6 nm was derived. Absorption bands were observed from 480 nm to 650 nm.
- (e) Pulsed laser photolysis-CRDS/UVS; both high resolution and broadband spectra reported. The high resolution spectrum shows no fine structure in the bands which are attributed to the $\text{OIO}(^2B_2\text{--}^2B_1)$ transition.
- (f) Same experimental conditions as in comment (d). Photofragment spectroscopy was used to study the quantum yield for $O(^3P)$ production and for $I(^2P_J)$ production

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following the photolysis of OIO at 532 nm. $O(^3P)$ was not detected, allowing the authors to put an upper limit of ~ 0.007 on the value of Φ_2 at 532 nm. $I(^2P_J)$ could not be detected in the single photon photolysis of OIO at 532 nm, and an upper limit of ~ 0.15 on the value of Φ_1 was derived.

5 Preferred Values

Absorption cross-sections

$$\sigma(\text{OIO}) = (2.7 \pm 1.6) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1} \text{ at } \lambda = 548.6 \text{ nm}$$

Quantum yields

$$\Phi_2 < 0.007 \text{ at } 532 \text{ nm}$$

10 Comments on Preferred Values

The absorption spectrum of OIO in the strong visible absorption band between ~ 480 nm and 660 nm is well established, but there is considerable disagreement between the absolute cross sections determined in the different studies, even when experimental errors and the effects of instrument resolution are accounted for. The values at 548.6 nm range from $(1.09 \pm 0.21) \times 10^{-17} \text{ cm}^2$ to $(3.5 \pm 1.5) \times 10^{-17} \text{ cm}^2$. The preferred absorption cross section is the lower limit value from the study of Ingham et al. (2000) and represents a compromise between the high and low values reported. The uncertainty covers the range of reported values.

15 Vibrational assignments of the $\tilde{A}-\tilde{X}$ band system and positions of the vibronic band centers between $15\,120 \text{ cm}^{-1}$ and $20\,753 \text{ cm}^{-1}$ (482 nm to 661 nm) are tabulated in Himmelmann et al. (1996).

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Dissociation of OIO into O(³P)+IO following absorption in the $\tilde{A}-\tilde{X}$ band system can be excluded on thermodynamic grounds. This is confirmed by the results of Ingham et al. (2000) who were unable to detect O atoms and report an upper limit of 0.007 for Φ_2 at 532 nm. Ingham et al. (2000) also report an upper limit of ~ 0.15 on the value of Φ_1 , but the results of Ashworth et al. (2002) provide compelling evidence that the ²B₂ upper state is strongly predissociated, and they report quantum calculations that efficient dissociation to I+O₂ can occur. This issue is unresolved and no recommendation is made for Φ_1 .

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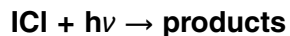
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Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
ICI + $h\nu$ → I + Cl	211	567
→ Cl($^2\text{P}_{1/2}$) + I	221	540
→ Cl + I($^2\text{P}_{1/2}$)	302	396

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–600	Seery and Britton, 1964	(a)
210–530	Jenkin et al., 1990	(b)

Quantum yield data

Wavelength/nm	Quantum Yield	Reference	Comments
235.3–237.8	$\Phi(\text{Cl}^*) = 0.40$	Tonokura et al., 1993	(c)
248	$\Phi(\text{I}^*) = 0.42$		

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Comments

- (a) Three measurements of the UV/Vis absorption spectrum have been performed in a 10 cm long quartz cell and the pressure was measured using a Pyrex spiral manometer. Runs with added Cl₂ indicated the disproportionation reaction to be immeasurably slow under the prevailing experimental conditions. The uncertainty in the absorption cross section was $\pm 0.2 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ throughout the wavelength range.
- (b) Spectrum of a static purified gas sample of ICl using a CCD camera over the wavelength range 210–690 nm. Good agreement with the spectrum of Seery and Britton (1964) except in the range 290–360 nm where the measured values of the cross sections seem to be lower than Seery and Britton (1964) presumably owing to a Cl₂ impurity. The value of the UV maximum $\sigma = 5 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ at 240 nm is slightly higher than in Seery and Britton (1964) by approximately 5–10%.
- (c) The stated relative quantum yields are consistent with the following measured concentration ratios observed in the diffusive molecular beam photodissociation experiment with REMPI detection of [Cl*] and [Cl] and two-photon laser-induced fluorescence of [I] and [I*], respectively: [Cl*]/[Cl]=0.68±0.10 in the range 235.3–237.8 nm and [I*]/[I]=0.71±0.27 at 248 nm. By inference the quantum yield for the ground state process is 0.18.

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Preferred Values

Absorption cross-sections at 298 K.

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
220	21.33	420	28.87
230	35.36	430	32.08
240	43.97	440	35.44
250	43.32	450	38.85
260	35.25	460	41.67
270	24.35	470	42.59
280	15.41	480	40.91
290	9.41	490	36.32
300	6.08	500	29.44
310	4.59	510	22.79
320	4.01	520	16.40
330	3.67	530	11.47
340	3.29	540	8.00
350	3.10	550	5.70
360	3.52	560	4.32
370	5.31	570	3.44
380	8.79	580	2.83
390	13.88	590	2.10
400	18.96	600	1.76
410	24.66		

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Comments on Preferred Values

The listed cross sections are the only ones available.

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- 5 Jenkin, M. E., Cox, R. A., Mellouki, A., Le Bras, G., and Poulet, G.: J. Phys. Chem., 94, 2927, 1990.
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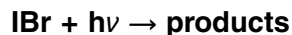
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Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
IBr + $h\nu$ → I + Br	178	672
→ Br($^2\text{P}_{1/2}$) + I	222	539
→ Br + I($^2\text{P}_{1/2}$)	269	445

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
220-600	Seery and Britton, 1964	(a)

Quantum yield data

Wavelength/nm	Quantum Yield	Reference	Comments
267	$\Phi(\text{Br}^*) = 0.35$	Kim et al., 1993	(b)
267	$\Phi(\text{I}^*) = 0.42$		
267	$\Phi(\text{I}) = 0.23$		
500	$\Phi(\text{Br}^*) = 0.73$	Haugen et al., 1985	(c)

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Comments

- (a) Four measurements of the UV/Vis absorption spectrum have been performed in a 10 cm long quartz cell and the pressure was measured using a Pyrex spiral manometer. Runs with added Br₂ indicated the disproportionation reaction to be unimportant under the prevailing experimental conditions. The uncertainty in the absorption cross section was $\pm 0.95 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ throughout the wavelength range.
- (b) The stated relative quantum yields are derived from the following measured concentration ratio observed in the diffusive molecular beam photodissociation experiment with REMPI detection of [Br*] and [Br], respectively, within the same laser pulse: [Br*]/[Br]=0.54 at 267 nm. Center-stripe analysis of velocity profiles affords the stated quantum yields for the channels yielding ground-state Br ($\Phi(I)=0.23$, $\Phi(I^*)=0.42$).
- (c) Approximate value resulting from a time-resolved laser gain vs. absorption spectroscopy technique.

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λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
220	3.59	420	31.73
230	5.70	430	44.77
240	10.21	440	58.69
250	16.71	450	71.92
260	21.45	460	85.18
270	23.09	470	98.49
280	21.10	480	111.10
290	16.82	490	119.86
300	12.43	500	121.66
310	7.95	510	115.92
320	5.39	520	103.08
330	3.36	530	85.83
340	2.14	540	67.52
350	1.45	550	52.34
360	1.53	560	36.63
370	2.37	570	27.22
380	4.17	580	19.88
390	6.96	590	14.57
400	12.04	600	11.32
410	20.46		

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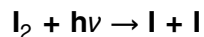
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Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{I}_2 + h\nu \rightarrow \text{I}({}^2\text{P}_{3/2}) + \text{I}({}^2\text{P}_{3/2})$	151	792

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
430–620	Rabinowitch and Wood, 1936a	(a)
420–800	Tellinghuisen, 1973	(b)
280–510	Bauer et al., 1998	(c)
180–750	Saiz-Lopez et al., 2004	(d)

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Quantum yield data

Wavelength/nm	Wavelength/nm	Reference	Comments
$\Phi = 1$	370–650	Rabinowitch and Wood, 1936b	(e)
$\Phi = 0.93 \pm 0.02$	501.0	Brewer and Tellinghuisen, 1972	(f)
$\Phi = 0.70 \pm 0.03$	509.1		
$\Phi = 0.62 \pm 0.02$	516.6		
$\Phi = 0.66 \pm 0.04$	527.7		
$\Phi = 0.72 \pm 0.02$	546.2		
$\Phi = 0.67 \pm 0.03$	559.4		
$\Phi = 0.59 \pm 0.03$	569.0		
$\Phi = 0.33 \pm 0.01$	589.6		
$\Phi = 0.35 \pm 0.01$	592.2		
$\Phi = 0.54 \pm 0.02$	603.7		
$\Phi = 0.67 \pm 0.04$	612.9		
$\Phi = 0.88 \pm 0.05$	623.9		

Comments

(a) The visible absorption spectrum was determined from measurements made at a series of wavelengths over the range 430–620 nm, at low resolution (5–10 nm), at room temperature (~ 293 K). Experiments were carried out using 0.2 mbar pure I_2 either in the absence of a bath gas, or in the presence of 670 mbar of He, air or Ar. Cross sections between 500–570 nm increased in the presence of the bath gases, but showed no dependence on bath gas identity. The cross section reported at the absorption maximum in the absence of a bath gas (i.e., close to 500 nm) was

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$\sim 2.8 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.

- (b) The visible-infrared absorption spectrum was determined from measurements made at 10 nm intervals over the wavelength range 420–800 nm, at a resolution of 0.26 nm. Measurements were made at room temperature (295–300 K) with pressures of purified I_2 of up to ~ 0.15 mbar. The cross section reported at 500 nm (the beginning of the $\text{B}^3\Pi \leftarrow \text{X}^1\Sigma$ continuum) was $(2.19 \pm 0.07) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.
- (c) The ultraviolet-visible absorption spectrum was recorded over the range 280–510 nm, at a resolution of 1.2 nm, with cross sections reported at 436 nm and 500 nm. Measurements were made at room temperature (295 ± 2 K) with pressures of purified I_2 up to 0.2 mbar. The cross section reported at 500 nm was $(2.25 \pm 0.09) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.
- (d) The ultraviolet-visible-infrared absorption spectrum was recorded using Fourier Transform spectroscopy over the wavelength range 182–750 nm, at a resolution of 0.036 nm in the banded region (500–650 nm) and 1 nm elsewhere. Measurements were made at room temperature (295 K) in 1.013 bar air. The absorption maximum was recorded in the banded region at 533 nm, with the cross section reported at 500 nm being $2.29 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.
- (e) Photodissociation quantum yields were determined from the reversible decrease in extinction during steady state illumination of I_2 vapour with a carbon arc or filament lamp. The use of appropriate filters allowed three broad band spectral regions to be considered for the photolysis radiation: ~ 370 –502 nm, $\lambda_{\text{max}} = 460$ nm; ~ 480 –590 nm, $\lambda_{\text{max}} = 502$ nm; ~ 503 –650 nm, $\lambda_{\text{max}} = 565$ nm. The quantum yield in the first region (essentially the $\text{B}^3\Pi \leftarrow \text{X}^1\Sigma$ continuum) was assumed to be unity. No significant difference in quantum yield for the other regions was observed. Experiments were carried out with 0.2 mbar I_2 in the presence of several hundred mbar of He, Ar, H_2 and N_2 .

5 (f) Photodissociation quantum yields were determined from fluorescence detection of $I(^2P_{3/2})$, during steady state photolysis of I_2 at 12 wavelengths, using a tungsten lamp in conjunction with combinations of interference filters. The transmittance bandwidth varied from 0.3 to 1.4 nm. The yields were determined relative to an assumed value of unity at 492 nm, in the $B^3\Pi \leftarrow X^1\Sigma$ continuum. Low pressure experiments were carried out with I_2 pressures up to ~ 0.01 mbar, to determine the zero pressure limiting quantum yields tabulated above. Experiments with up to 15 mbar N_2 demonstrated that the dissociative yield tends to unity in the presence of higher bath gas pressures.

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Absorption cross-sections for I₂ at 298 K.

λ/nm	$10^{18} \sigma/\text{cm}^2$	λ/nm	$10^{18} \sigma/\text{cm}^2$
400	0.029	565	1.54
405	0.038	570	1.28
410	0.043	575	0.955
415	0.053	580	0.912
420	0.058	585	0.729
425	0.081	590	0.644
430	0.133	595	0.588
435	0.153	600	0.466
440	0.199	605	0.422
445	0.253	610	0.400
450	0.327	615	0.336
455	0.432	620	0.300
460	0.560	625	0.276
465	0.709	630	0.274
470	0.880	635	0.220
475	1.07	640	0.233
480	1.29	645	0.222
485	1.52	650	0.212
490	1.75	655	0.203

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λ/nm	$10^{18} \sigma/\text{cm}^2$	λ/nm	$10^{18} \sigma/\text{cm}^2$
495	2.00	660	0.186
500	2.24	665	0.170
505	2.45	670	0.174
510	2.62	675	0.156
515	2.76	680	0.146
520	2.78	685	0.137
525	2.85	690	0.126
530	2.82	695	0.106
535	2.75	700	0.101
540	2.60	705	0.074
545	2.41	710	0.063
550	2.25	715	0.059
555	2.02	720	0.054
560	1.74	725	0.031

Quantum Yields

$\Phi = 1.0$ throughout the wavelength range.

Comments on Preferred Values

5 *Absorption Cross-Sections.* The visible-infrared absorption spectrum of I_2 has been the subject of a number of studies and discussions (Rabinowitch and Wood, 1936a; Calvert and Pitts, 1966; Tellinghuisen, 1973; Okabe, 1978; Bauer et al., 1998; Saiz-Lopez et al., 2004). The spectrum is dominated by the transition from the $X^1\Sigma$ ground state into the bound $B^3\Pi$ upper state, which results in rovibrational structure in the
 10 wavelength range 650–500 nm, with the dissociative continuum at ≤ 499 nm. There is

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also a weaker underlying continuum in the structured region, due to the transition to $^1\Pi$ repulsive state.

The shape of the absorption spectrum at wavelengths ≤ 500 nm (i.e. essentially in the continuum), based on a number of studies (Rabinowitch and Wood, 1936a; Tellinghuisen, 1973; Bauer et al., 1998; Saiz-Lopez et al., 2004), is well determined. Measurements in the structured region of the spectrum have been found to be very sensitive to experimental conditions, depending on the absolute concentration of I_2 and on pressure of bath gas, at the spectral resolutions typically employed. Cross sections averaged over a wavelength interval in this region should tend towards the true value when partial saturation of rotational lines is avoided though use of very low I_2 concentrations or at higher bath gas pressures when the lines become sufficiently broadened. The recent measurements of Saiz-Lopez et al. (2004), performed at high resolution and with high bath gas pressures, are therefore used to define the shape of the spectrum, with the preferred values based on their data averaged over 5 nm intervals.

The three most recent studies (Tellinghuisen, 1973; Bauer et al., 1998; Saiz-Lopez et al., 2004) report absorption cross sections in the pressure-independent continuum ($\lambda \leq 500$ nm) which are in excellent agreement, differing by less than 5% at 500 nm. The present recommendation therefore adopts a reference value of $\sigma = 2.24 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 500 nm, which is the average of the values reported in the three investigations.

Quantum Yields. The measurements of Rabinowitch and Wood (1936b) are consistent with a unity quantum yield throughout the visible-infrared spectrum at bath gas pressures greater than about 200 mbar. Brewer and Tellinghuisen (1972) report quantum yields well below unity in the structured region of the spectrum (501–624 nm) at low pressures in the absence of a bath gas, but observed significant increases (to >0.9) at N_2 pressures of only 15 mbar. The results of these studies are interpreted in terms of collision induced transition from the bound $B^3\Pi$ upper state into the unstable

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$^1\Pi$ repulsive state, leading to the generation of $I(^2P_{3/2})+I(^2P_{3/2})$, as does the weaker underlying continuum transition ($^1\Pi\leftarrow X^1\Sigma$). A quantum yield of unity throughout the spectrum is therefore recommended for lower atmospheric conditions. A number of studies have also determined quantum yields for the production of excited state $I(^2P_{1/2})$ atoms, which have been detected at wavelengths below ~ 530 nm (Hunter and Leong, 1987; and references therein). Under atmospheric conditions, collisional quenching of $I(^2P_{1/2})$ to ground state $I(^2P_{3/2})$ occurs rapidly.

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