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Evaluated kinetic and photochemical data for atmospheric chemistry: Volume IV – gas phase reactions of organic halogen species

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Abstract. This article, the fourth in the series, presents kinetic and photochemical data sheets evaluated by the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. It covers the gas phase and photochemical reactions of organic halogen species, which were last published in 1997, and were updated on the IUPAC website in 2006/07. The article consists of a summary sheet, containing the recommended kinetic parameters for the evaluated reactions, and four 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 In 1986 the IUPAC Subcommittee on Data Evaluation superseded the original CODATA Task Group for Atmospheric Chemistry, and the Subcommittee has continued its data evaluation program with Supplements published in 1989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 database with a search facility and implemented hyperlinks between the summary table and the data sheets, both of which can be downloaded as individual PDF or Word files. 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 fourth of the series, Volume IV.

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Summary of recommended rate coefficients for organic halogen 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). The reactions are numbered sequentially for the whole Volume. Within each family, reactions are listed in the order: $O(^3P)$, $O(^1D)$, halogen atom, HO radical, NO_3 radical, halogen oxide reactions and photochemical processes. 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 "IV.A1.1". Photochemical reactions are listed at the end of each family section.

Table 1. Summary of recommended rate coefficients for organic halogen reactions

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	$\Delta(E/R)/K^a$
FO_x Reactions - based on data sheets in Appendix 1, and on the IUPAC website updated in 2005.						
1	$O(^1D) + COF_2 \rightarrow O(^3P) + COF_2$	5.2×10^{-11}				
	$\rightarrow$ other products	2.2×10^{-11}				
	overall	7.4×10^{-11}	±0.3			
2	$O(^1D) + CH_3F \rightarrow O(^3P) + CH_3F$	2.7×10^{-11}				
	$\rightarrow$ other products	1.2×10^{-10}				
	overall	1.5×10^{-10}	±0.15			
3	$O(^1D) + CH_2F_2 \rightarrow O(^3P) + CH_2F_2$	3.6×10^{-11}				
	$\rightarrow$ other products	1.5×10^{-11}				
	overall	5.1×10^{-11}	±0.3			
4	$O(^1D) + CHF_3 \rightarrow O(^3P) + CHF_3$	8.2×10^{-12}				
	$\rightarrow$ other products	9.1×10^{-13}				
	overall	9.1×10^{-12}	±0.15			
5	$O(^1D) + CH_3CH_2F \rightarrow O(^3P) + CH_3CH_2F$	4.7×10^{-11}				
	$\rightarrow$ other products	2.1×10^{-10}				
	overall	2.6×10^{-10}	±0.3			
6	$O(^1D) + CH_3CHF_2 \rightarrow O(^3P) + CH_3CHF_2$	1.1×10^{-10}				
	$\rightarrow$ other products	9.2×10^{-11}				
	overall	2.0×10^{-10}	±0.3			
7	$O(^1D) + CH_3CF_3 \rightarrow O(^3P) + CH_3CF_3$					
	$\rightarrow$ other products	5.8×10^{-11}	±0.5			
8	$O(^1D) + CH_2FCF_3 \rightarrow O(^3P) + CH_2FCF_3$	4.6×10^{-11}				
	$\rightarrow$ other products	3.0×10^{-12}				
	overall	4.9×10^{-11}	±0.3			
9	$O(^1D) + CHF_2CF_3 \rightarrow O(^3P) + CHF_2CF_3$	1.0×10^{-10}				
	$\rightarrow$ other products	1.8×10^{-11}				
	overall	1.2×10^{-10}	±0.3			
10	$HO + CH_3F \rightarrow H_2O + CH_2F$	2.1×10^{-14}	± 0.15	$1.9 \times 10^{-12}\exp(-1350/T)$	240-300	±400
11	$HO + CH_2F_2 \rightarrow H_2O + CHF_2$	1.1×10^{-14}	± 0.10	$2.3 \times 10^{-12}\exp(-1590/T)$	220-300	±200
12	$HO + CHF_3 \rightarrow H_2O + CF_3$	2.7×10^{-16}	± 0.2	$6.9 \times 10^{-13}\exp(-2340/T)$	250-300	±300
13	$HO + CF_4 \rightarrow HOF + CF_3$	$< 2 \times 10^{-18}$				
14	$HO + CH_3CH_2F \rightarrow H_2O + CH_3CHF$	1.8×10^{-13}				
	$\rightarrow H_2O + CH_2CH_2F$	3.2×10^{-14}				
	overall	2.1×10^{-13}	± 0.2	$2.7 \times 10^{-12}\exp(-765/T)$	210-300	±300
15	$HO + CH_3CHF_2 \rightarrow H_2O + CH_2CHF_2$					
	$\rightarrow H_2O + CH_3CF_2$					
	overall	3.6×10^{-14}	$^{+0.10}_{-0.20}$	$1.25 \times 10^{-12}\exp(-1070/T)$	210-300	$^{+200}_{-400}$
16	$HO + CH_3CF_3 \rightarrow H_2O + CH_2CF_3$	1.2×10^{-15}	± 0.15	$9.2 \times 10^{-13}\exp(-1970/T)$	220-300	±300
17	$HO + CH_2FCH_2F \rightarrow H_2O + CH_2FCHF$	1.0×10^{-13}	± 0.3	$1.5 \times 10^{-12}\exp(-800/T)$	210-300	±200
18	$HO + CH_2FCHF_2 \rightarrow H_2O + CH_2FCF_2$					
	$\rightarrow H_2O + CHFCHF_2$					
	overall	1.5×10^{-14}	± 0.2	$3.3 \times 10^{-12}\exp(-1610/T)$	270-330	±300
19	$HO + CH_2FCF_3 \rightarrow H_2O + CHFCF_3$	4.6×10^{-15}	± 0.2	$4.9 \times 10^{-13}\exp(-1395/T)$	220-300	±300
20	$HO + CHF_2CHF_2 \rightarrow H_2O + CF_2CHF_2$	6.1×10^{-15}	± 0.2	$1.4 \times 10^{-12}\exp(-1620/T)$	290-360	±300
21	$HO + CHF_2CF_3 \rightarrow H_2O + CF_2CF_3$	1.9×10^{-15}	± 0.2	$4.4 \times 10^{-13}\exp(-1630/T)$	220-300	±300
22	$HO + CHF_2CF_2CH_2F \rightarrow H_2O + CHF_2CF_2CHF$					
	$\rightarrow H_2O + CF_2CF_2CH_2F$					
	overall	7.7×10^{-15}	± 0.3	$2.2 \times 10^{-12}\exp(-1685/T)$	285-365	±300
23	$HO + CF_3CF_2CH_2F \rightarrow H_2O + CF_3CF_2CHF$	6.5×10^{-15}	± 0.3	$2.6 \times 10^{-13}\exp(-1100/T)$	250-320	±400

Reaction number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k^a_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
24	$HO + CF_3CHFCHF_2 \rightarrow H_2O + CF_3CFCHF_2$						
	$\rightarrow H_2O + CF_3CHFCF_2$						
	overall	5.0×10^{-15}		$\pm$ 0.3	$1.4 \times 10^{-12}\exp(-1680/T)$	290-380	$\pm$300
25	$HO + CF_3CH_2CF_3 \rightarrow H_2O + CF_3CHCF_3$	3.3×10^{-16}		$\pm$ 0.3	$1.3 \times 10^{-12}\exp(-2465/T)$	270-340	$\pm$400
26	$HO + CF_3CHFCF_3 \rightarrow H_2O + CF_3CFCF_3$	1.4×10^{-15}		$\pm$ 0.2	$5.3 \times 10^{-13}\exp(-1770/T)$	250-380	$\pm$300
27	$HO + CHF_2OCHF_2 \rightarrow H_2O + CHF_2OCF_2$	2.2×10^{-15}		$\pm$ 0.1	$1.9 \times 10^{-12}\exp(-2020/T)$	270-460	$\pm$300
28	$HO + HCOF \rightarrow H_2O + FCO$	$< 1 \times 10^{-14}$					
29	$HO + CHF_2CHO \rightarrow H_2O + CHF_2CO$						
	$\rightarrow H_2O + CF_2CHO$						
	overall	1.6×10^{-12}		$\pm$ 0.2			
30	$HO + CF_3CHO \rightarrow H_2O + CF_3CO$	5.8×10^{-13}		$\pm$ 0.2			
31	$HO + CF_3COOH \rightarrow$ products	1.3×10^{-13}		$\pm$ 0.1	1.3×10^{-13}	280-350	$\Delta\log k = \pm0.1$
32	$HO_2 + CH_2FO_2 \rightarrow O_2 + CH_2FO_2H$	See data sheet					
	$\rightarrow O_2 + HCOF + H_2O$						
33	$HO_2 + CF_3O_2 \rightarrow CF_3O_2H + O_2$	no recommendation					
	$\rightarrow C(O)F_2 + HOF + O_2$						
34	$HO_2 + CF_3CHFO_2 \rightarrow O_2 + CF_3CHFO_2H$	4.3×10^{-12}		$\pm$ 0.2			
	$\rightarrow O_2 + CF_3C(O)F + H_2O$						
	overall	4.3×10^{-12}		$\pm$ 0.2	$2.0 \times 10^{-13}\exp(910)/T)$	210-365	$\pm$300
35	$HO_2 + CF_3CF_2O_2 \rightarrow O_2 + CF_3CF_2O_2H$						
	$\rightarrow O_2 + CF_3C(O)F + HOF$						
	overall	1.2×10^{-12}		$\pm$ 0.5			
36	$FO_2 + CO \rightarrow$ products	$< 6 \times 10^{-16}$					
37	$FO_2 + CH_4 \rightarrow$ products	$< 4.1 \times 10^{-15}$					
38	$CF_3 + O_2 + M \rightarrow CF_3O_2 + M$	2.2×10^{-29} $[N_2]$	(k_0)	$\pm$ 0.1	$2.2 \times 10^{-29}(T/300)^{-4.7}[N_2]$	230-380	$\Delta n = \pm1.5$
		4×10^{-12}	(k_∞)	$\pm$ 0.3	4×10^{-12}	200-300	$\Delta n = \pm1.5$
		$F_c = 0.39$			$F_c = 0.39$		
39	$CF_3O + O_2 \rightarrow COF_2 + FO_2$	$< 1 \times 10^{-18}$			$< 1 \times 10^{-10}\exp(-5600/T)$	250-370	
40	$CF_3O + O_3 \rightarrow CF_3O_2 + O_2$	1.8×10^{-14}		$\pm$1	$2 \times 10^{-12} \exp(-1400/T)$	250-370	$\pm$600
41	$CF_3O + H_2O \rightarrow CF_3OH + HO$	$< 2 \times 10^{-17}$			$< 3 \times 10^{-12} \exp(-3600/T)$	250-380	
42	$CF_3O + NO \rightarrow COF_2 + FNO$	5.4×10^{-11}		$\pm$ 0.1	$3.7 \times 10^{-11} \exp(110/T)$	230-390	$\pm$100
43	$CF_3O + CH_4 \rightarrow CF_3OH + CH_3$	2.2×10^{-14}		$\pm$ 0.1	$2.6 \times 10^{-12} \exp(-1420/T)$	230-380	$\pm$200
44	$CF_3O + C_2H_6 \rightarrow CF_3OH + C_2H_5$	1.3×10^{-12}		$\pm$ 0.1	$4.9 \times 10^{-12} \exp(-400/T)$	230-360	$\pm$200
45	$CH_2FO + O_2 \rightarrow HCOF + HO_2$				See data sheet		
46	$CH_2FO + M \rightarrow HCOF + H + M$				See data sheet		
47	$CH_3CF_2O + O_2 \rightarrow$ products				See data sheet		
48	$CH_3CF_2O + M \rightarrow CH_3 + COF_2 + M$				See data sheet		
49	$CH_2FCHFO + O_2 \rightarrow CH_2FCOF + HO_2$				See data sheet		
50	$CH_2FCHFO + M \rightarrow CH_2F + HCOF + M$				See data sheet		
51	$CF_3CHFO + O_2 \rightarrow CF_3COF + HO_2$				See data sheet		
52	$CF_3CHFO + M \rightarrow CF_3 + HCOF + M$				See data sheet		
53	$CF_3CF_2O + O_2 \rightarrow$ products				See data sheet		
54	$CF_3CF_2O + M \rightarrow CF_3 + CF_2O + M$				See data sheet		
55	$CH_2FO_2 + NO \rightarrow CH_2FO + NO_2$	1.3×10^{-11}		$\pm$ 0.3			
56	$CHF_2O_2 + NO \rightarrow CHF_2O + NO_2$	1.3×10^{-11}		$\pm$ 0.3			
57	$CF_3O_2 + NO \rightarrow CF_3O + NO_2$	1.6×10^{-11}		$\pm$ 0.1	$1.6 \times 10^{-11} \exp(T/298)^{-1.2}$	230-430	$\Delta n = \pm0.5$
58	$CH_2FCHFO_2 + NO$	$> 9 \times 10^{-12}$					
	$\rightarrow CH_2FCHFO + NO_2$						
59	$CHF_2CF_2O_2 + NO \rightarrow CHF_2CF_2O + NO_2$	$> 1 \times 10^{-11}$					
60	$CF_3CHFO_2 + NO \rightarrow CF_3CHFO + NO_2$	1.3×10^{-11}		$\pm$0.2			
61	$CF_3CF_2O_2 + NO \rightarrow CF_3CF_2O + NO_2$	$> 1 \times 10^{-11}$					
62	$CF_3O_2 + NO_2 + M \rightarrow CF_3O_2NO_2 + M$	$5.6 \times 10^{-29}[N_2]$	(k_0)	$\pm$0.2	5.6×10^{-29} $(T/298)^{-9}[N_2]$	260-300	$\Delta n = \pm3$
		7.7×10^{-12}	(k_∞)	$\pm$0.2	$7.7 \times 10^{-12}(T/298)^{-0.67}$	260-300	$\Delta n = \pm0.5$
		F_c=0.31			F_c=0.31	260-300	
63	$CF_3O_2NO_2 + M \rightarrow CF_3O_2 + NO_2 + M$	$4.5 \times 10^{-19}[N_2]$	(k_0/s^{-1})	$\pm$0.3	$2.5 \times 10^{-5}\exp(-9430/T)[N_2]$	260-300	$\pm$250
		6.0×10^{-2}	(k_∞/s^{-1})	$\pm$0.3	$1.5 \times 10^{16} \exp(-11940/T)$	260-300	$\pm$250
		F_c=0.31			F_c=0.31	260-300	
64	$CH_2FO_2 + CH_2FO_2$						
	$\rightarrow CH_2FOH + HC(O)F + O_2$						
	$\rightarrow 2CH_2FO + O_2$	2.6×10^{-12}		$\pm$0.3			
	overall	2.6×10^{-12}		$\pm$0.3	$2.5 \times 10^{-13}(\exp(700/T)$	220-380 $\pm$300	
65	$CHF_2O_2 + CHF_2O_2$						
	$\rightarrow CHF_2OH + C(O)F_2 + O_2$						
	$\rightarrow 2CH_2FO + O_2$	See data sheet					
	overall	$(2.5\text{-}5.0) \times 10^{-12}$					
66	$CF_3O_2 + CF_3O_2 \rightarrow 2CF_3O + O_2$	1.5×10^{-12}		$\pm$0.3			
67	$CF_3O_2 + CF_3CHFO_2$						
	$\rightarrow CF_3OH + CF_3COF + O_2$						
	$\rightarrow CF_3O + CF_3CHFO + O_2$						
	overall	8×10^{-12}		$\pm$0.5			
68	$CHF_2CF_2O_2 + CHF_2CF_2O_2$						
	$\rightarrow CHF_2CF_2O + CHF_2CF_2O + O_2$	no recommendation					

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	Δ (E/R)/K^a
69	$CF_3CHFO_2 + CF_3CHFO_2$					
	$\rightarrow CF_3CHFOH + CF_3COF + O_2$	3.3×10^{-13}				
	$\rightarrow 2\ CF_3CHFO + O_2$	4.4×10^{-12}				
	overall	4.7×10^{-12}	±0.3	$6.2 \times 10^{-13}\exp(605/T)$	210-375	±200
70	$CF_3CF_2O_2 + CF_3CF_2O_2$	no recommendation				
	$\rightarrow 2\ CF_3CF_2O + O_2$					
Data for the following Photochemical Reactions is based on data sheets on the IUPAC website updated in 2005						
71	$HC(O)F + h\nu \rightarrow$ products					
72	$C(O)F_2 + h\nu \rightarrow$ products					
73	$CF_3CHO + h\nu \rightarrow$ products					
74	$CF_3COF + h\nu \rightarrow$ products					
ClO_x Reactions - based on data sheets in Appendix 2, and on the IUPAC website updated in 2005						
75	$O(^1D) + CHF_2Cl \rightarrow O(^3P) + CHF_2Cl$	2.8×10^{-11}				
	$\rightarrow ClO + CHF_2$	5.5×10^{-11}				
	$\rightarrow$ other products	1.7×10^{-11}				
	overall	1.0×10^{-10}	±0.1	1×10^{-10}	170-350	$\Delta\log k=\pm0.1$
76	$O(^1D) + CHFCl_2 \rightarrow ClO + CHFCl$	1.4×10^{-10}				
	$\rightarrow$ other products	5.0×10^{-11}				
	overall	1.9×10^{-10}	±0.3	1.9×10^{-10}	180-350	$\Delta\log k=\pm0.3$
77	$O(^1D) + CH_3CF_2Cl \rightarrow O(^3P) + CH_3CF_2Cl$	5.7×10^{-11}				
	$\rightarrow$ other products	1.6×10^{-10}				
	overall	2.2×10^{-10}	±0.3			
78	$O(^1D) + CH_3CFCl_2 \rightarrow O(^3P) + CH_3CFCl_2$	8.1×10^{-11}				
	$\rightarrow$ other products	1.8×10^{-10}				
	overall	2.6×10^{-10}	±0.3			
79	$O(^1D) + CH_2ClCF_3 \rightarrow O(^3P) + CH_2ClCF_3$	2.4×10^{-11}				
	$\rightarrow$ other products	9.6×10^{-11}				
	overall	1.2×10^{-10}	±0.3			
80	$O(^1D) + CH_2ClCF_2Cl \rightarrow O(^3P) + CH_2ClCF_2Cl$	1.6×10^{-10}	±0.5			
	$\rightarrow$ other products					
81	$O(^1D) + CHFClCF_3 \rightarrow O(^3P) + CHFClCF_3$	2.7×10^{-11}				
	$\rightarrow$ other products	5.9×10^{-11}				
	overall	8.6×10^{-11}	±0.3			
82	$O(^1D) + CHCl_2CF_3 \rightarrow O(^3P) + CHCl_2CF_3$	4.2×10^{-11}				
	$\rightarrow$ other products	1.6×10^{-10}				
	overall	2.0×10^{-10}	±0.3			
83	$O(^1D) + CF_2Cl_2 \rightarrow ClO + CF_2Cl$	1.2×10^{-10}				
	$\rightarrow O(^3P) + CF_2Cl_2$	2.4×10^{-11}				
	overall	1.4×10^{-10}	±0.1	1.4×10^{-10}	170-350	$\Delta\log k=\pm0.1$
84	$O(^1D) + CFCl_3 \rightarrow ClO + CFCl_2$	2.0×10^{-10}				
	$\rightarrow O(^3P) + CFCl_3$	3.0×10^{-11}				
	overall	2.3×10^{-10}	±0.1	2.3×10^{-10}	170-350	$\Delta\log k=\pm0.1$
85	$O(^1D) + CCl_4 \rightarrow ClO + CCl_3$	2.9×10^{-10}				
	$\rightarrow O(^3P) + CCl_4$	4.0×10^{-11}				
	overall	3.3×10^{-10}	±0.1	3.3×10^{-10}	200-350	$\Delta\log k=\pm0.1$
86	$O(^1D) + COFCl \rightarrow O(^3P) + COFCl$	1.9×10^{-10}	±0.3			
87	$O(^1D) + COCl_2 \rightarrow O(^3P) + COCl_2$	See data sheet				
	$\rightarrow O(^3P) + Cl_2 + CO$	See data sheet				
	$\rightarrow$ other products	1.8×10^{-10}				
	overall	2.2×10^{-10}	±0.1	$2.0 \times 10^{-10}\exp(25/T)$	190-430	±25
88	$Cl + HC(O)Cl \rightarrow HCl + ClCO$	7.5×10^{-13}	±0.1	$8.1 \times 10^{-12}\exp(-710/T)$	220-330	±150
89	$Cl + CH_3OCl \rightarrow Cl_2 + CH_3O$	5.2×10^{-11}				
	$\rightarrow HCl + CH_2OCl$	9.15×10^{-12}				
	overall	6.1×10^{-11}	±0.1			
90	$Cl + CH_3F \rightarrow HCl + CH_2F$	3.5×10^{-13}	±0.15	$4.0 \times 10^{-12}\exp(-730/T)$	240-370	±400
91	$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$	4.8×10^{-13}	±0.1	$2.3 \times 10^{-11}\exp(-1150/T)$	220-360	±200
92	$Cl + CH_2F_2 \rightarrow HCl + CHF_2$	5.0×10^{-14}	±0.5	$7.0 \times 10^{-12}\exp(-1470/T)$	280-370	±500
93	$Cl + CH_2FCl \rightarrow HCl + CHFCl$	1.1×10^{-13}	±0.3	$7.0 \times 10^{-12}\exp(-1230/T)$	270-370	±500
94	$Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$	3.4×10^{-13}	±0.1	$5.9 \times 10^{-12}\exp(-850/T)$	220-400	±200
95	$Cl + CHF_2Cl \rightarrow HCl + CF_2Cl$	1.7×10^{-15}	±0.15	$5.9 \times 10^{-12}\exp(-2430/T)$	290-430	±400
96	$Cl + CHFCl_2 \rightarrow HCl + CFCl_2$	2.0×10^{-14}	±0.2	$5.5 \times 10^{-12}\exp(-1675/T)$	290-430	±400
97	$Cl + CHCl_3 \rightarrow HCl + CCl_3$	1.1×10^{-13}	±0.2	$2.4 \times 10^{-12}\exp(-920/T)$	220-500	±400
98	$Cl + CH_3CH_2F \rightarrow HCl + CH_3CHF$	6.5×10^{-12}	±0.3	$1.0 \times 10^{-11}\exp(-130/T)$	280-370	±500
	$\rightarrow HCl + CH_2CH_2F$	7.4×10^{-13}	±0.3	$8.3 \times 10^{-12}\exp(-720/T)$	280-370	±500
99	$Cl + CH_3CHF_2 \rightarrow HCl + CH_3CF_2$	2.5×10^{-13}	±0.15	$6.3 \times 10^{-12}\exp(-965/T)$	280-360	±500
	$\rightarrow HCl + CH_2CHF_2$	2.3×10^{-15}	±0.5	$7.0 \times 10^{-12}\exp(-2400/T)$	280-360	±500
100	$Cl + CH_2FCH_2F \rightarrow HCl + CH_2FCHF$	7.0×10^{-13}	±0.2	$2.5 \times 10^{-11}\exp(-1065/T)$	280-360	±400
101	$Cl + CH_3CF_3 \rightarrow HCl + CH_2CF_3$	2.6×10^{-17}	±0.5	$6.9 \times 10^{-12}\exp(-3720/T)$	280-370	±500
102	$Cl + CH_2FCHF_2 \rightarrow HCl + CH_2FCF_2$	2.5×10^{-14}	±0.5	$3.3 \times 10^{-12}\exp(-1450/T)$	280-370	±500
	$\rightarrow HCl + CHFCHF_2$	2.5×10^{-14}	±0.5	$4.6 \times 10^{-12}\exp(-1560/T)$	280-370	±500

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
103	$Cl + CH_3CF_2Cl \rightarrow HCl + CH_2CF_2Cl$	4.1×10^{-16}	±0.15	$1.4 \times 10^{-12}\exp(-2420/T)$	296-440	±500
104	$Cl + CH_3CFCl_2 \rightarrow HCl + CH_2CFCl_2$	2.1×10^{-15}	±0.1	$1.7 \times 10^{-12}\exp(-2000/T)$	290-380	±300
105	$Cl + CH_3CCl_3 \rightarrow HCl + CH_2CCl_3$	7×10^{-15}	±0.2	$2.8 \times 10^{-12}\exp(-1790/T)$	290-420	±400
106	$Cl + CH_2FCF_3 \rightarrow HCl + CHFCF_3$	1.5×10^{-15}	±0.1	$3.4 \times 10^{-12}\exp(-2300/T)$	299-430	±500
107	$Cl + CHF_2CHF_2 \rightarrow HCl + CF_2CHF_2$	2.2×10^{-15}	±0.2	$7.9 \times 10^{-12}\exp(-2440/T)$	280-360	±500
108	$Cl + CHF_2CF_3 \rightarrow HCl + CF_2CF_3$	2.5×10^{-16}	±0.2			
109	$Cl + CHFClCF_3 \rightarrow HCl + CFClCF_3$	2.7×10^{-15}	±0.1	$1.1 \times 10^{-12}\exp(-1800/T)$	270-380	±500
110	$Cl + CHCl_2CF_3 \rightarrow HCl + CCl_2CF_3$	1.2×10^{-14}	±0.1	$4.4 \times 10^{-12}\exp(-1740/T)$	270-380	±500
111	$HO + CH_3Cl \rightarrow H_2O + CH_2Cl$	3.6×10^{-14}	±0.10	$2.1 \times 10^{-12}\exp(-1210/T)$	220-300	±200
112	$HO + CH_2FCl \rightarrow H_2O + CHFCl$	3.9×10^{-14}	±0.1	$1.6 \times 10^{-12}\exp(-1105/T)$	240-300	±200
113	$HO + CH_2Cl_2 \rightarrow H_2O + CHCl_2$	1.0×10^{-13}	±0.10	$1.8 \times 10^{-12}\exp(-860/T)$	210-400	±150
114	$HO + CHF_2Cl \rightarrow H_2O + CF_2Cl$	4.7×10^{-15}	±0.08	$7.9 \times 10^{-13}\exp(-1530/T)$	240-300	±150
115	$HO + CHFCl_2 \rightarrow H_2O + CFCl_2$	2.9×10^{-14}	±0.1	$1.04 \times 10^{-12}\exp(-1065/T)$	240-300	±200
116	$HO + CHCl_3 \rightarrow H_2O + CCl_3$	1.05×10^{-13}	±0.10	$1.8 \times 10^{-12}\exp(-850/T)$	240-300	±300
117	$HO + CF_2Cl_2 \rightarrow HOCl + CF_2Cl$	$< 7 \times 10^{-18}$		$< 1 \times 10^{-12}\exp(-3540/T)$	250-480	
118	$HO + CFCl_3 \rightarrow HOCl + CFCl_2$	$< 5 \times 10^{-18}$		$< 1 \times 10^{-12}\exp(-3650/T)$	250-480	
119	$HO + CCl_4 \rightarrow HOCl + CCl_3$	$< 5 \times 10^{-16}$		$< 1 \times 10^{-12}\exp(-2260/T)$	250-300	
120	$HO + C_2HCl_3 \rightarrow$ products	2.0×10^{-12}	±0.10	$3.0 \times 10^{-13}\exp(565/T)$	230-300	±200
121	$HO + C_2Cl_4 \rightarrow$ products	1.6×10^{-13}	±0.10	$3.5 \times 10^{-12}\exp(-920/T)$	290-420	±300
122	$HO + CH_3CF_2Cl \rightarrow H_2O + CH_2CF_2Cl$	3.0×10^{-15}	±0.10	$8.5 \times 10^{-13}\exp(-1685/T)$	220-300	±200
123	$HO + CH_3CFCl_2 \rightarrow H_2O + CH_2CFCl_2$	5.8×10^{-15}	±0.10	$8.1 \times 10^{-13}\exp(-1470/T)$	220-300	±200
124	$HO + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$	9.5×10^{-15}	±0.10	$1.2 \times 10^{-12}\exp(-1440/T)$	240-300	±200
125	$HO + CH_2ClCF_3 \rightarrow H_2O + CHClCF_3$	1.4×10^{-14}	±0.15	$5.6 \times 10^{-13}\exp(-1100/T)$	260-380	±200
126	$HO + CH_2ClCF_2Cl \rightarrow H_2O + CHClCF_2Cl$	1.7×10^{-14}	±0.15	$3.5 \times 10^{-12}\exp(-1585/T)$	250-350	±300
127	$HO + CHFClCF_3 \rightarrow H_2O + CFClCF_3$	8.7×10^{-15}	±0.20	$3.5 \times 10^{-13}\exp(-1105/T)$	210-300	±300
128	$HO + CHCl_2CF_3 \rightarrow H_2O + CCl_2CF_3$	3.6×10^{-14}	±0.10	$6.6 \times 10^{-13}\exp(-870/T)$	210-300	±200
129	$HO + CHFClCF_2Cl \rightarrow H_2O + CFClCF_2Cl$	1.2×10^{-14}	±0.3	$8.4 \times 10^{-13}\exp(-1255/T)$	290-460	±400
130	$HO + CHCl_2CF_2Cl \rightarrow H_2O + CCl_2CF_2Cl$	5.1×10^{-14}	±0.2	$8.1 \times 10^{-13}\exp(-825/T)$	270-340	±200
131	$HO + CHFClCFCl_2 \rightarrow H_2O + CFClCFCl_2$	1.6×10^{-14}	±0.3	$5.8 \times 10^{-13}\exp(-1065/T)$	270-340	±400
132	$HO + CHCl_2CF_2CF_3 \rightarrow H_2O + CCl_2CF_2CF_3$	2.5×10^{-14}	±0.15	$1.1 \times 10^{-12}\exp(-1130/T)$	270-400	±300
133	$HO + CHFClCF_2CF_2Cl \rightarrow H_2O + CFClCF_2CF_2Cl$	8.9×10^{-15}	±0.10	$5.5 \times 10^{-13}\exp(-1230/T)$	290-400	±300
134	$HO + CH_3CF_2CFCl_2 \rightarrow H_2O + CH_2CF_2CFCl_2$	2.4×10^{-15}	±0.3	$7.0 \times 10^{-13}\exp(-1690/T)$	290-370	±300
135	$HO + HC(O)Cl \rightarrow H_2O + ClCO$	$< 5 \times 10^{-13}$				
136	$HO + CH_3OCl \rightarrow$ products	7.2×10^{-13}	±0.3	$2.4 \times 10^{-12}\exp(-360/T)$	250-350	±300
137	$HO + COCl_2 \rightarrow$ products	$< 5 \times 10^{-15}$				
138	$HO + CH_2ClCHO \rightarrow H_2O + CH_2ClCO$					
	$\rightarrow H_2O + CHClCHO$					
	overall	3.1×10^{-12}	±0.15			
139	$HO + CHFClCHO \rightarrow H_2O + CHFClCO$					
	$\rightarrow H_2O + CFClCHO$					
	overall	2.1×10^{-12}	±0.15			
140	$HO + CHCl_2CHO \rightarrow H_2O + CHCl_2CO$					
	$\rightarrow H_2O + CCl_2CHO$					
	overall	2.4×10^{-12}	±0.15			
141	$HO + CF_2ClCHO \rightarrow H_2O + CF_2ClCO$	8.2×10^{-13}	±0.25			
142	$HO + CFCl_2CHO \rightarrow H_2O + CFCl_2CO$	1.2×10^{-12}	±0.15			
143	$HO + CCl_3CHO \rightarrow H_2O + CCl_3CO$	8.0×10^{-13}	±0.15	$1.8 \times 10^{-12}\exp(-240/T)$	230-420	±200
144	$HO + CH_3COCl \rightarrow H_2O + CH_2COCl$	6.8×10^{-14}	±0.3			
145	$HO + CHF_2OCHClCF_3 \rightarrow H_2O + CHF_2OCClCF_3$					
	$\rightarrow H_2O + CF_2OCHClCF_3$					
	overall	1.5×10^{-14}	±0.10	$1.1 \times 10^{-12}\exp(-1280/T)$	250-430	±250
146	$HO + CHF_2OCF_2CHFCl \rightarrow H_2O + CHF_2OCF_2CFCl$					
	$\rightarrow H_2O + CF_2OCF_2CHFCl$					
	overall	1.2×10^{-14}	±0.10	$7.5 \times 10^{-13}\exp(-1230/T)$	250-430	±150
147	$HO_2 + CF_3CCl_2O_2 \rightarrow O_2 + CF_3CCl_2O_2H$	1.9×10^{-12}	±0.3			
148	$HO_2 + CH_2ClO_2 \rightarrow CH_2ClO_2H + O_2$					
	$\rightarrow HC(O)Cl + H_2O + O_2$					
	overall	5.0×10^{-12}	±0.3	$3.2 \times 10^{-13}\exp(820/T)$	250-600	±300
149	$HO_2 + CHCl_2O_2 \rightarrow CHCl_2O_2H + O_2$					
	$\rightarrow C(O)Cl_2 + H_2O + O_2$	4.1×10^{-12}				
	$\rightarrow HC(O)Cl + HOCl + O_2$	1.8×10^{-12}				
	overall	5.9×10^{-12}	±0.3	$5.6 \times 10^{-13}\exp(700/T)$	280-440	±300
150	$HO_2 + CF_2ClO_2 \rightarrow O_2 + CF_2ClO_2H$					
	$\rightarrow O_2 + COF_2 + HOCl$					
	$\rightarrow O_2 + FCOCl + HOF$					
	overall	3.4×10^{-12}	±0.5			
151	$HO_2 + CCl_3O_2 \rightarrow CCl_3O_2H + O_2$					
	$\rightarrow C(O)Cl_2 + HOCl + O_2$	5.1×10^{-12}				
	overall	5.1×10^{-12}	±0.3	$4.7 \times 10^{-13}\exp(710/T)$	280-440	±300
152	$HO_2 + CFCl_2CH_2O_2 \rightarrow O_2 + CFCl_2CH_2O_2H$					
	$\rightarrow O_2 + CFCl_2CHO + H_2O$					
	overall	9.2×10^{-12}	±0.5			
153	$HO_2 + CF_2ClCH_2O_2 \rightarrow O_2 + CF_2ClCH_2O_2H$					
	$\rightarrow O_2 + CF_2ClCHO + H_2O$					
	overall	6.8×10^{-12}	±0.5			

Reaction number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k^a_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
154	$NO_3 + C_2HCl_3 \rightarrow$ products	3.5×10^{-16}		±0.2	$3.2 \times 10^{-13}\exp(-2030/T)$	270-370	±500
155	$NO_3 + C_2Cl_4 \rightarrow$ products	$< 1 \times 10^{-16}$					
156	$ClO + CH_3O_2 \rightarrow ClOO + CH_3O$	1.6×10^{-12}			See data sheet		
	$\rightarrow OClO + CH_3O$						
	$\rightarrow HCHO + HCl + O_2$						
	$\rightarrow CH_3Cl + O_3$						
	$\rightarrow CH_3OCl + O_2$	3.3×10^{-13}			See data sheet		
	overall	2.2×10^{-12}		±0.15	$2.4 \times 10^{-12}\exp(-20/T)$	220-360	±200
157	$CF_2Cl + O_2 + M \rightarrow CF_2ClO_2 + M$	1.4×10^{-29} [N_2]	(k_0)	±0.5	$1.4 \times 10^{-29}(T/300)^{-5}[N_2]$	200-300	$\Delta n=\pm3$
		7×10^{-12}	(k_∞)	±0.5	$7 \times 10^{-12}(T/298)^{-0.6}$	200-300	$\Delta n=\pm0.5$
		$F_c= 0.4$			$F_c= 0.4$	200-300	
158	$CFCl_2 + O_2 + M \rightarrow CFCl_2O_2 + M$	6×10^{-30} [N_2]	(k_0)	±0.3	$6 \times 10^{-30}(T/298)^{-6}[N_2]$	230-380	$\Delta n=\pm3$
		9×10^{-12}	(k_∞)	±0.3	9×10^{-12}	230-300	$\Delta n=\pm1$
		$F_c \approx 0.4$			$F_c \approx 0.4$	230-380	
159	$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$	1.1×10^{-30} [N_2]	(k_0)	±0.2	$1.1 \times 10^{-30}(T/300)^{-6.2}[N_2]$	230-350	$\Delta n=\pm1$
		5.2×10^{-12}	(k_∞)	±0.3	$5.2 \times 10^{-12}(T/300)^{-1.4}$	260-350	$\Delta n=\pm1$
		$F_c= 0.35$			$F_c= 0.35$	230-350	
160	$CHFClO + O_2 \rightarrow COFCl + HO_2$				See data sheet		
161	$CHFClO + M \rightarrow HCOF + Cl + M$				See data sheet		
162	$CF_2ClO + O_2 \rightarrow$ products				See data sheet		
163	$CF_2ClO + M \rightarrow COF_2 + Cl + M$				See data sheet		
164	$CFCl_2O + O_2 \rightarrow$ products				See data sheet		
165	$CFCl_2O + M \rightarrow COFCl + Cl + M$				See data sheet		
166	$CCl_3O + M \rightarrow COCl_2 + Cl$				See data sheet		
167	$CF_2ClCH_2O + O_2 \rightarrow CF_2ClCHO + HO_2$				See data sheet		
168	$CF_2ClCH_2O + M \rightarrow CF_2Cl + HCHO + M$				See data sheet		
169	$CFCl_2CH_2O + O_2 \rightarrow CFCl_2CHO + HO_2$				See data sheet		
170	$CFCl_2CH_2O + M \rightarrow CFCl_2 + HCHO + M$				See data sheet		
171	$CF_3CFClO + O_2 \rightarrow$ products				See data sheet		
172	$CF_3CFClO + M \rightarrow CF_3COF + Cl + M$				See data sheet		
173	$CF_3CCl_2O + O_2 \rightarrow$ products				See data sheet		
174	$CF_3CCl_2O + M \rightarrow CF_3COCl + Cl + M$				See data sheet		
175	$CF_3CF_2CCl_2O + O_2 \rightarrow$ products				See data sheet		
176	$CF_3CF_2CCl_2O + M \rightarrow CF_3CF_2COCl + Cl + M$				See data sheet		
177	$CF_2ClCF_2CFClO + O_2 \rightarrow$ products				See data sheet		
178	$CF_2ClCF_2CFClO + M \rightarrow CF_2ClCF_2COF + Cl + M$				See data sheet		
179	$CH_2ClO + O_2 \rightarrow HCOCl + HO_2$				See data sheet		
180	$CH_2ClO + M \rightarrow HCO + HCl + M$				See data sheet		
181	$CH_3CHClO + O_2 \rightarrow CH_3COCl + HO_2$				See data sheet		
182	$CH_3CHClO + M \rightarrow CH_3CO + HCl + M$				See data sheet		
183	$HOCH_2CHClO + O_2 \rightarrow HOCH_2COCl + HO_2$				See data sheet		
184	$HOCH_2CHClO + M \rightarrow CH_2OH + HCOCl + M$				See data sheet		
185	$HOCHClCH_2O + O_2 \rightarrow HOCHClCHO + HO_2$				See data sheet		
186	$HOCHClCH_2O + M \rightarrow CHClOH + HCHO + M$				See data sheet		
187	$CH_3CCl_2O + O_2 \rightarrow$ products				See data sheet		
188	$CH_3CCl_2O + M \rightarrow CH_3COCl + Cl + M$				See data sheet		
189	$CCl_3CH_2O + O_2 \rightarrow CCl_3CHO + HO_2$				See data sheet		
190	$CCl_3CH_2O + M \rightarrow CCl_3 + HCHO + M$				See data sheet		
191	$CCl_3CCl_2O + O_2 \rightarrow$ products				See data sheet		
192	$CCl_3CCl_2O + M \rightarrow CCl_3COCl + Cl + M$				See data sheet		
193	$CH_2ClO_2 + NO \rightarrow CH_2ClO + NO_2$	1.9×10^{-11}		±0.3			
194	$CHFClO_2 + NO \rightarrow CHFClO + NO_2$	1.3×10^{-11}		±0.3			
195	$CF_2ClO_2 + NO \rightarrow CF_2ClO + NO_2$	1.5×10^{-11}		±0.2	$1.5 \times 10^{-11}(T/298)^{-1.5}$	230-430	$\Delta n=\pm0.5$
196	$CFCl_2O_2 + NO \rightarrow CFCl_2O + NO_2$	1.5×10^{-11}		±0.2	$1.5 \times 10^{-11}(T/298)^{-1.3}$	230-430	$\Delta n=\pm0.5$
197	$CCl_3O_2 + NO \rightarrow CCl_3O + NO_2$	1.8×10^{-11}		±0.2	$1.8 \times 10^{-11}(T/298)^{-1.0}$	230-430	$\Delta n=\pm0.5$
198	$CH_3CFClO_2 + NO \rightarrow CH_3CFClO + NO_2$	2.0×10^{-11}		±0.3	$2.0 \times 10^{-11}(T/298)^{-1.8}$	260-320	$\Delta n=\pm0.5$
199	$CF_2ClCH_2O_2 + NO \rightarrow CF_2ClCH_2O + NO_2$	1.2×10^{-11}		±0.3			
200	$CFCl_2CH_2O_2 + NO + M \rightarrow CFCl_2CH_2O + NO_2$	1.3×10^{-11}		±0.2	$1.3 \times 10^{-11}(T/298)^{-1.5}$	260-320	$\Delta n=\pm0.5$
201	$CF_3CCl_2O_2 + NO \rightarrow CF_3CCl_2O + NO_2$	1.8×10^{-11}		±0.3			
202	$CH_2ClCH_2O_2 + NO \rightarrow CH_2ClCH_2O + NO_2$	9.7×10^{-12}		±0.3			
203	$CF_2ClO_2 + NO_2 + M \rightarrow CF_2ClO_2NO_2 + M$	5.0×10^{-29} [N_2]	(k_0)	±0.3	$5.0 \times 10^{-29}(T/298)^{-6.2}[N_2]$	250-320	$\Delta n=\pm2$
		6.3×10^{-12}	(k_∞)	±0.3	$6.3 \times 10^{-12}(T/298)^{-0.7}$	250-320	$\Delta n=\pm0.5$
		$F_c=0.30$			$F_c=0.30$	250-320	
204	$CF_2ClO_2NO_2 + M \rightarrow CF_2ClO_2 + NO_2 + M$	9.0×10^{-19} [N_2]	(k_0/s^{-1})	±0.3	$1.8 \times 10^{-3}\exp(-10500/T)$ [N_2]	270-290	±200
		5.4×10^{-2}	(k_∞/s^{-1})	±0.3	$1.6 \times 10^{16}\exp(-11990/T)$	270-290	±200
		$F_c=0.30$			$F_c=0.30$	270-290	
205	$CFCl_2O_2 + NO_2 + M \rightarrow CFCl_2O_2NO_2 + M$	5.5×10^{-29} [N_2]	(k_0)	±0.3	$5.5 \times 10^{-29}(T/298)^{-5.5}$ [N_2]	230-380	$\Delta n=\pm2$
		8.3×10^{-12}	(k_∞)	±0.2	$8.3 \times 10^{-12}(T/298)^{-0.66}$	230-380	$\Delta n=\pm0.5$
		$F_c=0.42$			$F_c=0.42$	230-380	
206	$CFCl_2O_2NO_2 + M \rightarrow CFCl_2O_2 + NO_2 + M$	1.5×10^{-18} [N_2]	(k_0/s^{-1})	±0.3	$1.0 \times 10^{-2}\exp(-10860/T)[N_2]$	260-300	±200
		9.6×10^{-2}	(k_∞/s^{-1})	±0.3	$6.6 \times 10^{16}\exp(-12240/T)$	260-300	±500
		$F_c=0.28$			$F_c=0.28$	260-300	
207	$CCl_3O_2 + NO_2 + M \rightarrow CCl_3O_2NO_2 + M$	9.2×10^{-29} [N_2]	(k_0)	±0.3	$9.2 \times 10^{-29}(T/298)^{-6.0}$ [N_2]	230-380	$\Delta n=\pm2$
		1.5×10^{-12}	(k_∞)	±0.3	$1.5 \times 10^{-12}(T/298)^{-0.7}$	230-380	$\Delta n=\pm0.5$
		$F_c=0.32$			$F_c=0.32$	230-380	

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
208	$CCl_3O_2NO_2 + M \rightarrow CCl_3O_2 + NO_2 + M$	5.2×10^{-18} [N_2]	(k_0/s^{-1})	±0.3	$4.3 \times 10^{-3}\exp(-10235/T)[N_2]$	260-300	±500
		0.29	(k_∞/s^{-1})	±0.3	$4.8 \times 10^{16}\exp(-11820/T)$	260-300	±500
		F_c=0.32			F_c=0.32	260-300	
209	$C_2H_5O_2 + CF_3CCl_2O_2$						
	$\rightarrow CH_3CHO + CF_3CCl_2OH + O_2$	3.6×10^{-12}		±0.3			
	$\rightarrow C_2H_5O + CF_3CCl_2O + O_2$	9×10^{-13}		±0.5			
210	$CF_2ClCH_2O_2 + CF_2ClCH_2O_2$						
	$\rightarrow CF_2ClCH_2OH + CF_2ClCHO + O_2$						
	$\rightarrow CF_2ClCH_2O + CF_2ClCH_2O + O_2$	2.8×10^{-12}					
	overall	2.8×10^{-12}		±0.4			
211	$CFCl_2CH_2O_2 + CFCl_2CH_2O_2$						
	$\rightarrow CFCl_2CH_2OH + CFCl_2CHO + O_2$						
	$\rightarrow 2CFCl_2CH_2O + O_2$	2.9×10^{-12}					
	overall	2.9×10^{-12}		±0.4			
212	$CF_3CCl_2O_2 + CF_3CCl_2O_2$	3.5×10^{-12}		±0.3			
	$\rightarrow 2CF_3CCl_2O + O_2$						
213	$CH_2ClO_2 + CH_2ClO_2$						
	$\rightarrow CH_2ClOH + HC(O)Cl + O_2$						
	$\rightarrow 2CH_2ClO + O_2$	3.5×10^{-12}					
	overall	3.5×10^{-12}		±0.2	$1.9 \times 10^{-13}\exp(870/T)$	250-600	±200
214	$CHCl_2O_2 + CHCl_2O_2$	See data sheet					
	$\rightarrow CHCl_2OH + C(O)Cl_2 + O_2$						
	$\rightarrow CHCl_2O + CHCl_2O + O_2$						
215	$CCl_3O_2 + CCl_3O_2 \rightarrow 2CCl_3O + O_2$	4.0×10^{-12}		±0.3	$3.3 \times 10^{-13}\exp(740/T)$	270-460	±300
216	$CH_3CHClO_2 + CH_3CHClO_2$						
	$\rightarrow CH_3CHClOH + CH_3COCl + O_2$						
	$\rightarrow 2CH_3CHClO + O_2$	5×10^{-12}		±0.3			
	overall	See data sheet					
217	$CH_2ClCH_2O_2 + CH_2ClCH_2O_2$						
	$\rightarrow CH_2ClCH_2OH + CH_2ClCHO + O_2$	1.2×10^{-12}					
	$\rightarrow 2CH_2ClCH_2O + O_2$	2.1×10^{-12}					
	overall	3.3×10^{-12}		±0.3	$4.2 \times 10^{-14}\exp(1300/T)$	220-380	±500
218	$O_3 + C_2HCl_3 \rightarrow$ products	$< 5 \times 10^{-20}$					
219	$O_3 + C_2Cl_4 \rightarrow$ products	$< 10^{-21}$					
Data for the following Photochemical Reactions is based on data sheets on the IUPAC website updated in 2005							
220	$CH_3Cl + h\nu \rightarrow$ products						
221	$CH_3OCl + h\nu \rightarrow$ products						
222	$CHF_2Cl + h\nu \rightarrow$ products						
223	$CF_2Cl_2 + h\nu \rightarrow$ products						
224	$CFCl_3 + h\nu \rightarrow$ products						
225	$CCl_4 + h\nu \rightarrow$ products						
226	$CH_3CF_2Cl + h\nu \rightarrow$ products						
227	$CH_3CFCl_2 + h\nu \rightarrow$ products						
228	$CH_3CCl_3 + h\nu \rightarrow$ products						
229	$CF_3CHFCl + h\nu \rightarrow$ products						
230	$CF_3CHCl_2 + h\nu \rightarrow$ products						
231	$CF_2ClCFCl_2 + h\nu \rightarrow$ products						
232	$CF_2ClCF_2Cl + h\nu \rightarrow$ products						
233	$CF_3CF_2Cl + h\nu \rightarrow$ products						
234	$CF_3CF_2CHCl_2 + h\nu \rightarrow$ products						
235	$CF_2ClCF_2CHFCl + h\nu \rightarrow$ products						
236	$HCOCl + h\nu \rightarrow$ products						
237	$COFCl + h\nu \rightarrow$ products						
238	$COCl_2 + h\nu \rightarrow$ products						
239	$CF_2ClCHO + h\nu \rightarrow$ products						
240	$CFCl_2CHO + h\nu \rightarrow$ products						
241	$CCl_3CHO + h\nu \rightarrow$ products						
242	$CF_3COCl + h\nu \rightarrow$ products						
BrO_x Reactions - based on data sheets in Appendix 3, and on the IUPAC website updated in 2005							
243	$HO + CH_3Br \rightarrow H_2O + CH_2Br$	2.9×10^{-14}		±0.08	$1.7 \times 10^{-12}\exp(-1215/T)$	240-300	±150
244	$HO + CH_2Br_2 \rightarrow H_2O + CHBr_2$	1.1×10^{-13}		±0.15	$1.5 \times 10^{-12}\exp(-775/T)$	240-300	±200
245	$HO + CHF_2Br \rightarrow H_2O + CF_2Br$	1.0×10^{-14}		±0.10	$7.9 \times 10^{-13}\exp(-1300/T)$	230-360	±150
246	$HO + CF_3Br \rightarrow$ products	$< 6.0 \times 10^{-18}$			$< 1 \times 10^{-12}\exp(-3600/T)$	250-460	
247	$HO + CF_2ClBr \rightarrow$ products	$< 1 \times 10^{-17}$			$< 1 \times 10^{-12}\exp(-3450/T)$	250-380	
248	$HO + CF_2Br_2 \rightarrow$ products	$< 5.0 \times 10^{-16}$			$< 1 \times 10^{-12}\exp(-2200/T)$	250-460	
249	$HO + CF_3CH_2Br \rightarrow H_2O + CF_3CHBr$	1.6×10^{-14}		±0.2	$1.4 \times 10^{-12}\exp(-1340/T)$	280-460	±300
250	$HO + CF_3CHFBr \rightarrow H_2O + CF_3CFBr$	1.7×10^{-14}		±0.2	$8.1 \times 10^{-13}\exp(-1155/T)$	270-460	±300
251	$HO + CF_3CHClBr \rightarrow H_2O + CF_3CClBr$	4.6×10^{-14}		±0.20	$1.2 \times 10^{-12}\exp(-970/T)$	290-460	±300
252	$HO + CF_2BrCF_2Br \rightarrow$ products	$< 6 \times 10^{-18}$			$< 1 \times 10^{-12}\exp(-3600/T)$	250-460	
253	$HO_2 + CH_2BrO_2 \rightarrow O_2 + CH_2BrO_2H$	6.7×10^{-12}					
	$\rightarrow O_2 + HC(O)Br + H_2O$						
254	$CH_2BrO_2 + NO \rightarrow CH_2BrO + NO_2$	1.1×10^{-11}		±0.3			
255	$CHBr_2O_2 + NO \rightarrow CHBr_2O + NO_2$	1.7×10^{-11}		±0.3			

Reaction number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	Δlog k_{298}^a	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
256	$CH_2BrO_2 + CH_2BrO_2$					
	$\rightarrow HC(O)Br + CH_2BrOH + O_2$	see data sheet				
	$\rightarrow 2CH_2BrO + O_2$					
257	$BrCH_2CH_2O_2 + BrCH_2CH_2O_2$					
	$\rightarrow BrCH_2CH_2OH + BrCH_2CHO + O_2$	1.7×10^{-12}				
	$\rightarrow 2BrCH_2CH_2O + O_2$	2.3×10^{-12}				
	overall	4.0×10^{-12}	±0.2	6.0×10^{-14}exp(1250/T)	270-380	±500
258	$BrO + CH_3O_2 \rightarrow CH_3O + BrOO$	1.4×10^{-12}				
	$\rightarrow HOBr + CH_2O_2$	4.3×10^{-12}				
	overall	5.7×10^{-12}	± 0.3			
Data for the following Photochemical Reactions is based on data sheets on the IUPAC website updated in 2006						
259	$CH_3Br + h\nu \rightarrow$ products					
260	$CF_3Br + h\nu \rightarrow$ products					
261	$CF_2ClBr + h\nu \rightarrow$ products					
262	$CF_2Br_2 + h\nu \rightarrow$ products					
263	$CHBr_3 + h\nu \rightarrow$ products					
264	$CF_2BrCF_2Br + h\nu \rightarrow$ products					
265	$CH_2Br_2 + h\nu \rightarrow$ products					
IO_x Reactions – based on data data sheets in Appendix 4, and on the IUPAC website updated in 2005						
266	$HO + CH_3I \rightarrow H_2O + CH_2I$	1.0×10^{-13}	±0.2	4.3×10^{-12}exp(-1120/T)	270-430	±500
267	$HO + CF_3I \rightarrow$ products	2.6×10^{-14}	±0.2	2.1×10^{-11}exp(-2000/T)	270-370	±500
268	$CH_2IO_2 + CH_2IO_2 \rightarrow CH_2IOH + HC(O)I + O_2$	no recommendation				
	$\rightarrow 2CH_2IO + O_2$					
Data for the following Photochemical Reactions is based on data sheets on the IUPAC website updated in 2006						
269	$CH_3I + h\nu \rightarrow$ products					
270	$CF_3I + h\nu \rightarrow$ products					
271	$CH_2ClI + h\nu \rightarrow$ products					
272	$CH_2BrI + h\nu \rightarrow$ products					
273	$CH_2I_2 + h\nu \rightarrow$ products					

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

2 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.

2.1 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, which is provided on the IUPAC website.

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, generally 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 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
REMPI - resonance enhanced multiphoton ionisation
RF – resonance fluorescence
RR – relative rate
S – static system
TDLS – tunable diode laser spectroscopy
UV – ultraviolet
UVA – ultraviolet absorption
VUVA – vacuum ultraviolet absorption

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

The preferred rate coefficients are presented (i) at a temperature of 298 K and (ii) in temperature dependent form over a stated temperature range. This is followed by a statement of the uncertainty limits in log k at 298 K and the uncertainty limits either in (E/R) or in n, for the mean temperature in the range. Some comments on the assignment of uncertainties are given later in this Introduction.

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

2.2 Conventions concerning rate coefficients

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

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

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

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

2.3 Treatment of combination and dissociation reactions

Unlike simple bimolecular reactions such as those considered in Sect. 3.2, combination reactions

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

and the reverse dissociation reactions

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

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:

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

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

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

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

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,

$$\mathrm{A + B \rightarrow AB^*} \quad (1)$$

$$\mathrm{AB^* \rightarrow A + B} \quad (-1)$$

$$\mathrm{AB^* + M \rightarrow AB + M} \quad (2)$$

while the dissociation reactions are characterized by:

$$\mathrm{AB + M \rightarrow AB^* + M} \quad (-2)$$

$$\mathrm{AB^* + M \rightarrow AB + M} \quad (2)$$

$$AB^* \rightarrow A + B \qquad (-1)$$

Assuming quasi-stationary concentrations for the highly excited unstable species AB^* (i.e. that $d[AB^*]/dt \approx 0$), 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:

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

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.

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

$$k = \frac{k_o k_\infty}{k_o + k_\infty}$$

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 $K_c = k_1 k_2 / k_{-1} k_{-2}$.

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):

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

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 $N \approx [0.75 - 1.27 \log F_c]$. 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=200–300 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 $HO+NO_2$, 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 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

$$\mathrm{A} + \mathrm{M} \rightarrow \mathrm{AM} \tag{3}$$

$$\mathrm{AM} \rightarrow \mathrm{A} + \mathrm{M} \tag{-3}$$

$$\mathrm{B} + \mathrm{AM} \rightarrow \mathrm{AB} + \mathrm{M} \tag{4}$$

which, in the low pressure range, leads to

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

For some tri- and tetra-atomic adducts AB, e.g. O + O_2 → O_3 and Cl + O_2 → ClOO, this value of k_0 may exceed that from the energy-transfer mechanism and show stronger temperature as dependencies (Luther et al., 2005). 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=N_2, O_2 or air.

2.4 Treatment of complex-forming bimolecular reactions

Bimolecular reactions may follow the "direct" pathway

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

and/or involve complex formation,

$$\begin{array}{l} \mathrm{A} + \mathrm{B} \Leftrightarrow \mathrm{AB}^* \rightarrow \mathrm{C} + \mathrm{D} \\ \qquad\qquad\ \downarrow \mathrm{M} \\ \qquad\qquad\ \mathrm{AB} \end{array}$$

We designate the rate coefficients of the individual steps as in Sect. 3.3, above:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB}^* \tag{1}$$

$$\mathrm{AB}^* \rightarrow \mathrm{A} + \mathrm{B} \tag{-1}$$

$$\mathrm{AB}^* + \mathrm{M} \rightarrow \mathrm{AB} + \mathrm{M} \tag{2}$$

$$\mathrm{AB}^* \rightarrow \mathrm{C} + \mathrm{D} \tag{3}$$

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

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

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

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -(k_S + k_D)[\mathrm{A}][\mathrm{B}]$$

where

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

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

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 to account for the multistep character of process (2) and the energy and angular momemtum dependencies of processes (1), (-1) and (3). These broadening factors, however, differ from those for combination and dissociation reactions. For simplicity, they are ignored in this evaluation such that k_D at high pressure approaches

$$k_D \rightarrow k_1k_3/k_2$$

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

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

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]. One should also note that bimolecular reactions may have contributions from direct as well as complex-forming pathways leading to identical or different products.

2.5 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: $\log_{10}(\sigma_{T1}/\sigma_{T2})=\mathrm{B}(T_1\text{-}T_2)$ is used.

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

2.6 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:

$$\mathrm{I}/\mathrm{I}_0=\exp(-\sigma[\mathrm{N}]l),$$

$$\sigma=\{1/([\mathrm{N}]l)\}\ln(\mathrm{I}_0/\mathrm{I}),$$

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

2.7 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, $\log k=c\pm d$. This is equivalent to the statement that k is uncertain to a factor of f, where $d=\log f$. The accuracy of the preferred value of E/R is quoted as the term $\Delta(E/R)$, where $\Delta(E/R)=g$ and g is defined by the equation $E/R=h\pm g$. d and g are expanded uncertainties corresponding approximately to a 95% confidence limit.

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

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

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 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 95% confidence limits, of ±10% or less are frequently reported in the literature. Unfortunately, when evaluators 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 free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise.

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.

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 reliable data. Thus, we do not feel justified at present in assigning uncertainty limits to the parameters reported for the photochemical reactions.

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DATASHEETS

Appendix 1: FO_x Reactions

IV.A1.1

$$\begin{aligned} \mathbf{O(^1D) + COF_2} &\rightarrow \mathbf{O(^3P) + COF_2} \quad \mathbf{(1)} \\ &\rightarrow \textbf{other products} \quad \mathbf{(2)} \end{aligned}$$

$\Delta H°(1)$ = -190 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.4 \pm 1.2) \times 10^{-11}$	298	Wine and Ravishankara, 1983	PLP-RF
Branching Ratios			
$k_1/k = 0.7 \pm 0.07$	298	Wine and Ravishankara, 1983	PLP-RF (a)

Comments

(a) Branching ratio was determined from the ratio of the $O(^3P)$ yield from $O(^1D) + COF_2$ relative to that for $O(^1D) + N_2$.

Preferred Values

$k = 7.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.7$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value of k is based on the result of Wine and Ravishankara (1983). This study is much more direct than earlier studies. In that paper the authors state that the only chemical reaction involving COF_2 which might be important in the stratosphere is the reaction $O(^1D) + COF_2 \rightarrow F_2 + CO_2$ and that this reaction would have to proceed by a complex mechanism involving an intermediate adduct.

References

Wine, P. H. and Ravishankara, A. R.: Chem. Phys. Lett., 96, 129, 1983.

IV.A1.2

$$\mathbf{O(^1D) + CH_3F \rightarrow O(^3P) + CH_3F \quad (1)}$$
$$\mathbf{\rightarrow \text{other products} \quad (2)}$$

$\Delta H^\circ(1)$ = -190 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.38 \pm 0.06) \times 10^{-10}$	298	Force and Wiesenfeld, 1981	PLP-RA
$(1.65 \pm 0.15) \times 10^{-10}$	298	Schmoltner et al., 1993	PLP-RF
Branching Ratios			
$k_1/k = 0.25 \pm 0.03$	298	Force and Wiesenfeld, 1981	PLP-RA (a)
$k_1/k = 0.11 \pm 0.05$	298	Schmoltner et al., 1993	PLP-RF (b)
$k_1/k = 0.19 \pm 0.05$	298	Takahashi et al., 1996	PLP-LIF (b)

Comments

(a) $O(^1D)$ atoms were monitored by resonance absorption at 130.4 nm and compared to $O(^3P)$ atoms in the presence of ozone in He diluent where the $O(^3P)$ atom yield from the $O(^1D) + O_3$ reaction is 1.0.

(b) Branching ratio was determined from the ratio of the $O(^3P)$ yield from $O(^1D) + CH_3F$ relative to that for $O(^1D) + N_2$.

Preferred Values

$k = 1.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.18$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (k_1/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value of k is the average of the values reported by Force and Wiesenfeld (1981) and by Schmoltner et al. (1993). The preferred value of the branching ratio k_1/k is the average of the values reported by Force and Wiesenfeld (1981), Schmoltner et al. (1993) and Takahashi et al. (1996). In these experiments, only $O(^3P)$ was monitored and therefore no direct information relating to the products of the chemical reaction of $O(^1D) + CH_3F$ was obtained. Burks and Lin (1981) have observed the appearance of stimulated emissions from vibrationally excited HF. Park and Wiesenfeld (1991) observed some production of HO, but they reported that HF elimination dominates over HO production.

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Takahashi, K., Wada, R., Matsumi, Y. and Kawasaki, M.: J. Phys. Chem., 100, 10145, 1996.

IV.A1.3

$$\mathbf{O(^1D) + CH_2F_2 \rightarrow O(^3P) + CH_2F_2} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow \text{other products}} \quad \mathbf{(2)}$$

$\Delta H°(1)$ = -190 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.13 \pm 0.33) \times 10^{-11}$	298	Schmoltner et al., 1993	PLP-RF
Branching Ratios			
$k_1/k = 0.70 \pm 0.11$	298	Schmoltner et al., 1993	PLP-RF (a)

Comments

(a) Branching ratio was determined from the ratio of the O(^{3}P) yield from O(^{1}D) + CH_2F_2 relative to that for O(^{1}D) + N_2.

Preferred Values

$k = 5.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.70$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred value of k and the preferred value of the branching ratio k_1/k are based on the results of Schmoltner et al. (1993). In these experiments, only O(^{3}P) was monitored and therefore no direct information relating to the products of the chemical reaction of O(^{1}D) + CH_2F_2 was obtained. Burks and Lin (1981) have observed the appearance of stimulated emissions from vibrationally excited HF.

References

Burks, T. L. and Lin, M. C.: Int. J. Chem. Kinet., 13, 977, 1981.
Schmoltner, A. M., Talukdar, R. K., Warren, R. F., Mellouki, A., Goldfarb, L., Gierczak, T., McKeen, S. A. and Ravishankara, A. R.: J. Phys. Chem., 97, 8976, 1993.

IV.A1.4

$$\mathbf{O(^1D) + CHF_3 \rightarrow O(^3P) + CHF_3 \quad (1)}$$
$$\mathbf{\rightarrow \text{other products} \quad (2)}$$

$\Delta H°(1)$ = -190 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.4 \pm 0.8) \times 10^{-12}$	298	Force and Wiesenfeld, 1981	PLP-RA
$(9.76 \pm 0.60) \times 10^{-12}$	298	Schmoltner et al., 1993	PLP-RF
Branching Ratios			
$k_1/k = 0.77 \pm 0.15$	298	Force and Wiesenfeld, 1981	PLP-RA (a)
$k_1/k = 1.02 \pm 0.15$	298	Schmoltner et al., 1993	PLP-RF (b)

Comments

(a) $O(^1D)$ atoms were monitored by resonance absorption at 130.4 nm and compared to $O(^3P)$ atoms in the presence of ozone in He diluent where the $O(^3P)$ atom yield from the $O(^1D) + O_3$ reaction is 1.0.

(b) Branching ratio was determined from the ratio of the $O(^3P)$ yield from $O(^1D) + CHF_3$ relative to that for $O(^1D) + N_2$.

Preferred Values

$k = 9.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.9$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (k_1/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value of k is the average of the values reported by Force and Wiesenfeld (1981) and Schmoltner et al. (1993). The preferred value of the branching ratio k_1/k is the average of the values reported by Force and Wiesenfeld (1981) and Schmoltner et al. (1993). In these experiments, only $O(^3P)$ was monitored and therefore no direct information relating to the products of the chemical reaction of $O(^1D) + CHF_3$ was obtained. Burks and Lin (1981) and Aker et al. (1987) have observed the appearance of stimulated emissions from vibrationally excited HF.

References

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IV.A1.5

$$\mathbf{O(^1D) + CH_3CH_2F \rightarrow O(^3P) + CH_3CH_2F \quad (1)}$$
$$\mathbf{\rightarrow \text{other products} \quad (2)}$$

$\Delta H°(1) = -190\ \text{kJ·mol}^{-1}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.61 \pm 0.40) \times 10^{-10}$	298	Schmoltner et al., 1993	PLP-RF
Branching Ratios			
$k_1/k = 0.18 \pm 0.05$	298	Schmoltner et al., 1993	PLP-RF (a)

Comments

(a) Branching ratio was determined from the ratio of the $O(^3P)$ yield from $O(^1D) + CH_3CH_2F$ relative to that for $O(^1D) + N_2$.

Preferred Values

$k = 2.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.18$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value of k and the branching ratio k_1/k are based on the results of Schmoltner et al. (1993), the only published study of this reaction. In these experiments, only $O(^3P)$ was monitored and therefore no direct information relating to the products of the chemical reaction of $O(^1D) + CH_3CH_2F$ was obtained.

References

Schmoltner, A. M., Talukdar, R. K., Warren, R. F., Mellouki, A., Goldfarb, L., Gierczak, T., McKeen, S. A. and Ravishankara, A. R.: J. Phys. Chem., 97, 8976, 1993.

IV.A1.6

$$\mathbf{O(^1D) + CH_3CHF_2 \rightarrow O(^3P) + CH_3CHF_2 \quad (1)}$$
$$\mathbf{\rightarrow \text{other products} \quad (2)}$$

$\Delta H°(1)$ = -190 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.02 \pm 0.15) \times 10^{-10}$	298	Warren et al., 1991	PLP-RF
Branching Ratios			
$k_1/k = 0.54 \pm 0.07$	298	Warren et al., 1991	PLP-RF (a)

Comments

(a) Branching ratio was determined from the ratio of the O(^{3}P) yield from O(^{1}D) + CH_3CHF_2 relative to that for O(^{1}D) + N_2.

Preferred Values

$k = 2.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.54$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value of k and the preferred value of the branching ratio k_1/k are based on the results of Warren et al. (1991), the only published study of this reaction. In these experiments, only O(^{3}P) was monitored and therefore no direct information relating to the products of the chemical reaction of O(^{1}D) + CH_3CHF_2 was obtained.

References

Warren, R., Gierczak, T. and Ravishankara, A. R.: Chem. Phys. Lett., 183, 403, 1991.

IV.A1.7

$$\mathbf{O(^1D) + CH_3CF_3 \rightarrow O(^3P) + CH_3CF_3 \quad (1)}$$
$$\mathbf{\rightarrow \text{other products} \quad (2)}$$

$\Delta H^\circ(1)$ = -190 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$k_2 = (5.8 \pm 2.0) \times 10^{-11}$	297	Green and Wayne, 1976	RR (a)

Comments

(a) O(^{1}D) produced by photolysis of NO_2 at 229 nm. $\Delta(CH_3CF_3)/\Delta(N_2O)$ monitored by IR absorption spectroscopy. Measured rate coefficient ratio of $k_2/k(O(^1D) + N_2O) = 0.5 \pm 0.1$ is placed on an absolute basis by use of $k(O(^1D) + N_2O) = 1.16 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current evaluation). The cited rate coefficient refers to chemical reaction only and does not include physical quenching.

Preferred Values

$k_2 = 5.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$

Comments on Preferred Values

The preferred value of k_2 is derived from the relative rate results reported by Green and Wayne (1976) in the only published study of this reaction. It should be noted that this rate coefficient refers to chemical reaction only and does not include physical quenching of O(^{1}D).

References

Green, R. G. and Wayne, R. P.: J. Photochem. 6, 371, 1976.
IUPAC, http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.

IV.A1.8

$$\begin{aligned} \mathbf{O(^1D) + CH_2FCF_3} \quad &\rightarrow \mathbf{O(^3P) + CH_2FCF_3} \quad &\mathbf{(1)} \\ &\rightarrow \mathbf{other\ products} \quad &\mathbf{(2)} \end{aligned}$$

$\Delta H°(1) = -190\ kJ{\cdot}mol^{-1}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.85 \pm 0.25) \times 10^{-11}$	298	Warren et al., 1991	PLP-RF
Branching Ratios			
$k_1/k = 0.94^{+0.06}_{-0.10}$	298	Warren et al., 1991	PLP-RF (a)

Comments

(a) Branching ratio was determined from the ratio of the $O(^3P)$ yield from $O(^1D) + CH_2FCF_3$ relative to that for $O(^1D) + N_2$.

Preferred Values

$k = 4.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.94$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = (^{+0.06}_{-0.10})$ at 298 K.

Comments on Preferred Values

The preferred value of k and the preferred value of the branching ratio k_1/k are based on the results of Warren et al. (1991), the only published study of this reaction. In these experiments, only $O(^3P)$ was monitored and therefore no direct information relating to the products of the chemical reaction of $O(^1D) + CH_2FCF_3$ was obtained.

References

Warren, R., Gierczak, T. and Ravishankara, A. R.: Chem. Phys. Lett., 183, 403, 1991.

IV.A1.9

$$\mathbf{O(^1D) + CHF_2CF_3 \rightarrow O(^3P) + CHF_2CF_3 \quad (1)}$$
$$\mathbf{\rightarrow \text{other products} \quad (2)}$$

$\Delta H°(1) = -190\ \mathrm{kJ{\cdot}mol^{-1}}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.23 \pm 0.06) \times 10^{-10}$	298	Warren et al., 1991	PLP-RF
Branching Ratios			
$k_1/k = 0.85\ ^{+0.15}_{-0.22}$	298	Warren et al., 1991	PLP-RF (a)

Comments

(a) Branching ratio was determined from the ratio of the $O(^3P)$ yield from $O(^1D) + CHF_2CF_3$ relative to that for $O(^1D) + N_2$.

Preferred Values

$k = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.85$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = (^{+0.15}_{-0.3})$ at 298 K.

Comments on Preferred Values

The preferred value of k and the preferred value of the branching ratio k_1/k are based on the results of Warren et al. (1991). In these experiments, only $O(^3P)$ was monitored and therefore no direct information relating to the products of the chemical reaction of $O(^1D) + CHF_2CF_3$ was obtained.

References

Warren, R., Gierczak, T. and Ravishankara, A. R.: Chem. Phys. Lett., 183, 403, 1991.

IV.A1.10

$$\mathbf{HO + CH_3F \rightarrow H_2O + CH_2F}$$

ΔH° = -78.2 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.60 \pm 0.35) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
$(2.18 \pm 0.18) \times 10^{-14}$	297	Nip et al., 1979	FP-RA
$8.11 \times 10^{-12} \exp[-(1887 \pm 61)/T]$	292-480	Jeong et al., 1984	DF-RF (a)
$(1.40 \pm 0.09) \times 10^{-14}$	292		
$(1.71 \pm 0.24) \times 10^{-14}$	298	Bera and Hanrahan, 1988	PR-A
$1.75 \times 10^{-12} \exp[-(1300 \pm 100)/T]$	243-373	Schmoltner et al., 1993	PLP/FP-LIF
$(2.09 \pm 0.08) \times 10^{-14}$	298		
Relative Rate Coefficients			
$(1.71 \pm 0.08) \times 10^{-14}$	296 ± 2	Wallington and Hurley, 1993	RR (b)
$(1.41 \pm 0.07) \times 10^{-14}$	296 ± 2	Wallington and Hurley, 1993	RR (c)
$(1.32 \pm 0.12) \times 10^{-14}$	295	Møgelberg et al., 1994	RR (d)
$2.77 \times 10^{-18} T^2 \exp[-(754 \pm 34)/T]$	298-363	Hsu and DeMore, 1995	RR (e)
1.96×10^{-14}	298		
$4.21 \times 10^{-18} T^2 \exp[-(856 \pm 82)/T]$	308-393	DeMore, 1996	RR (f)

Comments

(a) The rate expression cited in Jeong et al. (1984) supersedes that reported in Jeong and Kaufman (1982). Jeong et al. (1984) also corrects an erroneously reported rate measurement at 480 K.

(b) HO radicals were generated by photolysis of CH_3ONO at 933 mbar total pressure of air. The decay of CH_3F was inferred from the measured formation of HC(O)F, using a formation yield of HC(O)F of 0.90 as measured in separate Cl_2-CH_3F-NO-air irradiations. The concentrations of HC(O)F and acetylene were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3F)/k(HO + C_2H_2) = 0.0201 \pm 0.0009$ was placed on an absolute basis by using $k(HO + C_2H_2) = 8.49 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 296 K and 1013 mbar air (Sørensen et al. 2003).

(c) HO radicals generated by the photolysis of O_3 at 254 nm in the presence of H_2. The concentrations of CH_4 and CH_3F were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3F)/k(HO + CH_4) = 2.30 \pm 0.11$ was placed on an absolute basis by using $k(HO + CH_4) = 6.14 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

(d) HO radicals generated by the photolysis of O_3 at 254 nm in the presence of H_2. The decay of CH_4 and CH_3F concentrations was monitored by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3F)/k(HO + CH_4) = 2.2 \pm 0.2$ was placed on an absolute basis by using $k(HO + CH_4) = 6.01 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 295 K (IUPAC, current recommendation).

(e) HO radicals were generated by the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or O_3-H_2O)-CH_3F-CH_3CHF_2-O_2-N_2 mixtures. The concentrations of CH_3F and CH_3CHF_2 were measured by IR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3F)/k(HO + CH_3CHF_2) = (0.99 \pm 0.10) \exp[-(174 \pm 34)/T]$ is placed on an absolute basis by using a rate coefficient of $k(HO + CH_3CHF_2) = 2.80 \times 10^{-18} T^2 \exp(-580/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(f) HO radicals generated by the photolysis of O_3 at 254 nm in the presence of H_2O vapour. The decay of CH_3Cl and CH_3F concentrations was monitored by FTIR spectroscopy. The rate coefficient ratio of $k(HO + CH_3F)/k(HO + CH_3Cl)$ = (0.97

± 0.23) exp[-(156 ± 82)/T] was measured over the temperature range 308-393 K. The rate coefficient ratio was placed on an absolute basis by using k(HO + CH_3Cl) = 4.34 × 10^{-18} T^2 exp(-700/T) cm^3 $molecule^{-1}$ s^{-1} (IUPAC, current recommendation).

Preferred Values

k = 2.1 × 10^{-14} cm^3 $molecule^{-1}$ s^{-1} at 298 K.
k = 1.9 x 10^{-12} exp(-1350/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 240-300 K.

Reliability

Δ log k = ± 0.15 at 298 K.
Δ (E/R) = ± 400 K.

Comments on Preferred Values

The absolute rate coefficients of Schmoltner et al. (1993) are higher than those reported previously by Jeong and Kaufman (1982) and Jeong et al. (1984), although the discrepancy decreases with increasing temperature. The absolute rate coefficients of Schmoltner et al. (1993), although exhibiting scatter at temperatures $\leq$ 273 K, are in good agreement with the relative rate coefficients of Hsu and DeMore (1995) and DeMore (1996) at 298 K and above. The absolute rate coefficient of Nip et al. (1979) is in good agreement with the data of Schmoltner et al. (1993), Hsu and DeMore (1995) and DeMore (1996). Because secondary reactions of HO radicals with CH_2F radicals and other radical species were expected to have occurred in the study of Bera and Hanrahan (1988), their rate coefficient was consequently not used in the evaluation. The absolute rate coefficients of Howard and Evenson (1976), Jeong and Kaufman (1982), Wallington and Hurley (1993), and Møgelberg et al. (1994) appear to be systematically lower than other studies, and therefore they were not used in the evaluation.

The data of Nip et al. (1979), Schmoltner et al. (1993), Hsu and DeMore (1995) and DeMore (1996) were fitted to the three-parameter equation $k = CT^2$ exp(-D/T), resulting in k = 3.66 × 10^{-18} T^2 exp(-818/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 243-393 K. The preferred Arrhenius expression, $k = A$ exp(-B/T), is centered on a mid-range temperature, T_m, of 265 K and is derived from the three parameter equation with $A = C\ e^2\ T_m^2$ and $B = D + 2T_m$.

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IV.A1.11

$HO + CH_2F_2 \rightarrow H_2O + CHF_2$

$\Delta H°$ = -65.0 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.8 \pm 1.2) \times 10^{-15}$	296	Howard and Evenson, 1976	DF-LMR
$7.42 \times 10^{-12} \exp[-(2100 \pm 200)/T]$	293-429	Clyne and Holt, 1979	DF-RF
$(5.8 \pm 0.3) \times 10^{-15}$	293		
$(1.17 \pm 0.14) \times 10^{-14}$	297	Nip et al., 1979	FP-RA
$4.4 \times 10^{-12} \exp[-(1766 \pm 50)/T]$	250-492	Jeong et al., 1984	DF-RF (a)
$(1.12 \pm 0.075) \times 10^{-14}$	298		
$(8.8 \pm 1.4) \times 10^{-15}$	298	Bera and Hanrahan, 1988	PR-A
$1.57 \times 10^{-12} \exp[-(1470 \pm 100)/T]$	222-381	Talukdar et al., 1991	FP-LIF
$(1.13 \pm 0.01) \times 10^{-14}$	298		
$(2.52 \pm 0.25) \times 10^{-15}$	223	Schmoltner et al., 1993	PLP/FP-LIF
$(1.09 \pm 0.03) \times 10^{-14}$	298		
$(1.00 \pm 0.03) \times 10^{-14}$	298	Szilagyi et al., 2000	DF-RF
Relative Rate Coefficients			
$2.24 \times 10^{-18} T^2 \exp[-(857 \pm 24)/T]$	297-383	Hsu and DeMore, 1995	RR (b)
1.12×10^{-14}	297		

Comments

(a) The rate expression cited in Jeong et al. (1984) supersedes that reported in Jeong and Kaufman (1982).

(b) Relative rate method. HO radicals were generated from the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or O_3-H_2O)-CH_2F_2-CH_3CHF_2-O_2-N_2 mixtures. The concentrations of CH_2F_2 and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_2F_2)/k(HO + CH_3CHF_2) = (0.80 \pm 0.06) \exp[-(277 \pm 24)/T]$ is placed on an absolute basis using a rate coefficient of $k(HO + CH_3CHF_2) = 2.80 \times 10^{-18} T^2 \exp(-580/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.3 \times 10^{-12} \exp(-1590/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-300 K.

Reliability

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

Comments on Preferred Values

The absolute rate coefficients of Schmoltner et al. (1993) at 223 K and 298 K are in excellent agreement with the earlier and much more extensive rate coefficient data of Talukdar et al. (1991). The room temperature rate coefficients of Nip et al. (1983), Jeong and Kaufman (1982), Jeong et al. (1984), Talukdar et al. (1991) and Schmoltner et al. (1993) are in good agreement, but are ∼ 30% higher than those of Howard and Evenson (1976), Clyne and Holt (1979) and Bera and Hanrahan (1988). The data of Clyne and Holt (1979) are not considered reliable and that of Bera and Hanrahan (1988) may have been subject to secondary reactions. The rate coefficients measured by Jeong and Kaufman (1982) (250–492 K) and Talukdar et al. (1991) (222–381 K) are in good agreement over the temperature range where they overlap.

The rate coefficient data of Nip et al. (1983), Jeong and Kaufman (1982), Talukdar et al. (1991), Hsu and DeMore (1995), Schmoltner et al. (1993), and Szilagyi et al. (2000) have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 4.80 \times 10^{-18}\ T^2 \exp(-1080/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 222–492 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered on a mid-range temperature, T_m, of 255 K and is derived from the three parameter equation with $A = C\ \mathrm{e}^2\ T_m^2$ and $B = D + 2T_m$.

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IV.A1.12

$HO + CHF_3 \rightarrow H_2O + CF_3$

ΔH° = -47.5 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.2) \times 10^{-16}$	296	Howard and Evenson, 1976	DF-LMR
$(1.3 \pm 0.4) \times 10^{-15}$	296	Clyne and Holt, 1979	DF-RF
$(1.4 \pm 0.6) \times 10^{-15}$	430		
$(3.49 \pm 1.66) \times 10^{-16}$	297	Nip et al., 1979	FP-RA
2.98×10^{-12} exp[-(2908 ± 156)/T]	387-480	Jeong et al., 1984	DF-RF (a)
1.71×10^{-16}	298		(b)
$(2.3 \pm 0.4) \times 10^{-15}$	298	Bera and Hanrahan, 1988	PR-RA
6.93×10^{-13} exp[-(2300 ± 100)/T]	252-374	Schmoltner et al., 1993	FP-LIF
$(3.08 \pm 0.28) \times 10^{-16}$	298		
1.1×10^{-12} exp[-(2300 ± 207)/T]	298-753	Medhurst et al., 1997	PLP-LIF
$(1.5 \pm 0.2) \times 10^{-16}$	298		
Relative Rate Coefficients			
1.05×10^{-18} T^2 exp[-(1774 ± 44)/T]	298-383	Hsu and DeMore, 1995	RR (c)
2.42×10^{-16}	298		
6.19×10^{-19} T^2 exp[-(1523 ± 34)/T]	253-343	Chen et al., 2003	RR (d,e)
3.32×10^{-16}	298		
1.12×10^{-18} T^2 exp[-(1706 ± 44)/T]	253-343	Chen et al., 2003	RR (d,f)
3.25×10^{-16}	298		

Comments

(a) The rate expression cited in Jeong et al. (1984) supersedes that reported in Jeong and Kaufman (1982). Jeong et al. (1984) also corrects an erroneously reported rate measurement at 465 K.

(b) Extrapolated value.

(c) Relative rate method. HO radicals were generated from the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or H_2O-O_3)-CHF_3-CHF_2CF_3-N_2-O_2 mixtures. The concentrations of CHF_3 and CHF_2CF_3 were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + CHF_3)/k(HO + CHF_2CF_3) = (1.14 ± 0.08) exp[-(654 ± 44)/T] is placed on an absolute basis by using a rate coefficient of k(HO + CHF_2CF_3) = 9.24×10^{-19} T^2 exp(-1120/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(d) Relative rate method. HO radicals were generated from the photolysis of H_2O at 254 nm in the presence of a continuous flow of a 3% O_3 in O_2 mixture. The concentrations of CHF_3 and reference compounds were measured by GC-FID. Total initial reactor pressure was 266 mbar (200 Torr) with the pressure rising to 400–666 mbar (300–500 Torr) at the end of an experiment.

(e) Relative to CHF_2CF_3. An Arrhenius plot of the Chen et al. (2003) data gives a rate coefficient ratio of k(HO + CHF_3)/k(HO + CHF_2CF_3) = (0.67 ± 0.12) exp[-(403 ± 34)/T] over the temperature range 253–343 K. The rate coefficient ratio was placed on an absolute basis by using a rate coefficient of k(HO + CF_3CHF_2) = 9.24×10^{-19} T^2 exp(-1120/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(f) Relative to CHF_2Cl. An Arrhenius plot of the Chen et al. (2003) data gives a rate coefficient ratio of k(HO + CHF_3)/k(HO + CHF_2Cl) = (0.74 ± 0.17) exp[-(706 ± 44)/T] over the temperature range 253–343 K. The rate coefficient ratio was placed on an absolute basis by using a rate coefficient of k(HO + CHF_2Cl) = 1.52 $\times$ 10^{-18} T^2 exp(-1000/T) cm^3 $molecule^{-1}$ s^{-1} (IUPAC, current recommendation).

Preferred Values

k = 2.7 $\times$ 10^{-16} cm^3 $molecule^{-1}$ s^{-1} at 298 K.
k = 6.9 $\times$ 10^{-13} exp(-2340/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 250-300 K.

Reliability

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

Comments on Preferred Values

The absolute rate coefficient study of Schmoltner et al. (1993) and the relative rate studies of Chen et al. (2003) are the only temperature-dependent studies carried out at temperatures below 298 K. The rate coefficients of Schmoltner et al. (1993) and Chen et al. (2003) are in very good agreement over the temperature range 252–343 K. The rate coefficients from the relative rate study of Hsu and DeMore (1995) are $\sim$ 10-20% lower than the absolute rate coefficients of Schmoltner et al. (1993) and the relative rate studies of Chen et al. (2003) over the temperature range common to all studies, with the disagreement increasing with decreasing temperature. However, the absolute rate coefficients of Jeong and Kaufmann (1982) are in good agreement with the relative rate coefficients of Hsu and DeMore (1995) at temperatures 383–387 K. The data of Medhurst et al. (1997) were obtained at temperatures predominantly above room temperature. Moreover, the rate coefficients calculated from the Arrhenius fit to their experimental data are substantially higher than any other study. Therefore, the data of Medhurst et al. (1997) were not used in the evaluation. The rate coefficient of Nip et al. (1979) is in good agreement with the data of Schmoltner et al. (1993) and Chen et al. (2003), but the rate coefficient of Howard and Evenson (1976) is $\sim$ 40% lower. The data of Clyne and Holt (1979) and Bera and Hanrahan (1988) were not used due to their inconsistency with the other data.

The absolute rate coefficients of Howard and Evenson (1976), Nip et al. (1979), Jeong and Kaufman (1982), Schmoltner et al. (1993) and the relative rate coefficients of Chen et al. (2003) have been fitted to the three parameter equation k = CT^2 exp(-D/T), resulting in k = 1.42 $\times$ 10^{-18} T^2 exp(-1798/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 252–480 K. The preferred Arrhenius expression, k = A exp(-B/T), is centered on a mid-range temperature, T_m, of 270 K and is derived from the three parameter equation with A = C e^2 T_m^2 and $B = D + 2T_m$. The relative rate data of Hsu and DeMore (1995) are $\sim$ 10% lower than the preferred values.

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IV.A1.13

$$\mathbf{HO + CF_4 \rightarrow HOF + CF_3}$$

$\Delta H° = 327.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<4 \times 10^{-16}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$<1 \times 10^{-15}$	293	Clyne and Holt, 1979	DF-RF
$<2 \times 10^{-18}$	∼298	Ravishankara et al., 1993	PLP-LIF (a)

Comments

(a) Not explicitly reported, but expected to be a pulsed photolysis system with LIF detection of HO radicals as carried out by Schmoltner et al. (1993) for HO radical reaction rate coefficient measurements with related hydrofluorocarbons.

Preferred Values

$k < 2 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is the upper limit to the rate coefficient reported by Ravishankara et al. (1993).

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IV.A1.14

$$\mathbf{HO + CH_3CH_2F \rightarrow H_2O + CH_3CHF \quad (1)}$$
$$\mathbf{\rightarrow H_2O + CH_2CH_2F \quad (2)}$$

$\Delta H°(1) = -74.4\ \mathrm{kJ{\cdot}mol^{-1}}$
$\Delta H°(2) = -59.6\ \mathrm{kJ{\cdot}mol^{-1}}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.32 \pm 0.37) \times 10^{-13}$	297 ± 2	Nip et al., 1979	FP-RA
$2.69 \times 10^{-12} \exp[-(750 \pm 100)/T]$	243-373	Schmoltner et al., 1993	PLP/FP-LIF
$(2.17 \pm 0.29) \times 10^{-13}$	298		
$6.78 \times 10^{-12} \exp[-(1033 \pm 74)/T]$	298-480	Kozlov et al., 2003	FP-RF
$2.42 \times 10^{-12} \exp[-(716 \pm 36)/T]$	210-298		
$(2.20 \pm 0.03) \times 10^{-13}$	298		
Relative Rate Coefficients			
$1.73 \times 10^{-17}\ T^2 \exp[-(657 \pm 36)/T]$	285-364	Hsu and DeMore, 1995	RR (a)
1.69×10^{-13}	298		

Comments

(a) HO radicals were generated by the photolysis of H_2O at 185 nm or of H_2O-O_3 mixtures in the UV in H_2O (or H_2O-O_3)-CH_3CH_2F-C_2H_6-O_2-N_2 mixtures. The concentrations of CH_3CH_2F and C_2H_6 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3CH_2F)/k(HO + C_2H_6) = (1.16 \pm 0.13) \exp[-(158 \pm 36)/T]$ is placed on an absolute basis using a rate coefficient of $k(HO + C_2H_6) = 1.49 \times 10^{-17}\ T^2 \exp(-499/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 2.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.7 \times 10^{-12} \exp(-765/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210-300 K.
$k_1/k = 0.85$ K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 300$ K.
$k_1/k = \pm 0.15$ at 298 K.

Comments on Preferred Values

The rate coefficients of Nip et al. (1979), Schmoltner et al. (1993) and Kozlov et al. (2003) are in good agreement over the temperature range 243-373 K. The relative rate coefficients of Hsu and DeMore (1995) display a higher temperature dependence compared to that observed by Schmoltner et al. (1993) and Kozlov et al. (2003). At room temperature, the rate coefficients of Hsu and DeMore (1995) are ∼35% lower than those of Nip et al. (1979), Schmoltner et al. (1993) and Kozlov et al. (2003). The source of the disagreement is not known although impurities in the reactant were ruled out in the Kozlov et al. (2003) study. Above 298 K (329–364 K), the agreement between the data of Hsu and DeMore (1995), Schmoltner et al. (1993) and Kozlov et al. (2003) is better.

The study by Kozlov et al. (2003) shows curvature in the Arrhenius plot. Singleton et al. (1980) determined that 85% of the abstraction by HO is from the CH_2F group at 298 K. Therefore, at least some of the observed curvature is probably due to the increasing importance of H atom abstraction from the unsubstituted methyl group (CH_3) with increasing temperature.

The absolute rate coefficients of Nip et al. (1979), Schmoltner et al. (1993) and Kozlov et al. (2003) were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 6.12 \times 10^{-18}\ T^2 \exp(-275/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210–480 K. The preferred Arrhenius expression $k = A \exp(-B/T)$, is centered on a mid-range temperature, T_m, of 245 K and is derived from the three parameter equation with $A = C\, e^2\, T_m^2$ and $B = D + 2T_m$. The relative rate data of Hsu and DeMore (1995) are approximately 20-30% lower than the preferred value at 298 K.

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IV.A1.15

$$\mathbf{HO + CH_3CHF_2 \rightarrow H_2O + CH_2CHF_2} \quad (1)$$
$$\mathbf{\rightarrow H_2O + CH_3CF_2} \quad (2)$$

$\Delta H°(1) = -53.8$ kJ·mol^{-1}
$\Delta H°(2) = -69.8$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.12 \pm 0.70) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
$(3.50 \pm 0.50) \times 10^{-14}$	293	Handwerk and Zellner, 1978	FP-RA
$2.92 \times 10^{-12} \exp[-(1200 \pm 100)/T]$	293-417	Clyne and Holt, 1979	DF-RF
$(4.66 \pm 0.16) \times 10^{-14}$	293		
$(3.7 \pm 0.4) \times 10^{-14}$	297 ± 2	Nip et al., 1979	FP-RA
$1.42 \times 10^{-12} \exp[-(1050)/T]$	220-423	Brown et al. 1990	DF-RF
4.2×10^{-14}	298		
$9.6 \times 10^{-13} \exp[-(940 \pm 130)/T]$	270-400	Liu et al., 1990	FP-RF
$(4.22 \pm 0.45) \times 10^{-14}$	298		
$1.0 \times 10^{-12} \exp[-(980 \pm 50)/T]$	212-349	Gierczak et al., 1991	DF-LMR/FP-LIF
$(3.76 \pm 0.6) \times 10^{-14}$	293		
$3.9 \times 10^{-12} \exp[-(1370 \pm 260)/T]$	295-388	Nielsen, 1991	PR-RA
$(4.7 \pm 1.1) \times 10^{-14}$	295		
$3.24 \times 10^{-12} \exp[-(1372 \pm 89)/T]$	298-480	Kozlov et al., 2003	FP-RF
$9.36 \times 10^{-13} \exp[-(998 \pm 56)/T]$	210-298		
$(3.38 \pm 0.05) \times 10^{-14}$	298		
Relative Rate Coefficients			
$(3.86 \pm 0.67) \times 10^{-14}$	298 ± 2	DeMore, 1992	RR (a)
$(3.45 \pm 0.34) \times 10^{-14}$	298 ± 2	DeMore, 1992	RR (b)
$3.44 \times 10^{-18}\, T^2 \exp[-(690 \pm 57)/T]$	298-358	Hsu and DeMore, 1995	RR (c)
3.02×10^{-14}	298		
$1.18 \times 10^{-20}\, T^{2.82} \exp[-(388 \pm 67)/T]$	298-358	Hsu and DeMore, 1995	RR (b)
3.05×10^{-14}	298		
$2.53 \times 10^{-18}\, T^2 \exp[-(557 \pm 19)/T]$	286-403	Wilson et al., 2003	RR (d,e)
3.47×10^{-14}	298		
$1.22 \times 10^{-18}\, T^2 \exp[-(329 \pm 42)/T]$	290-391	Wilson et al., 2003	RR (d,f)
3.59×10^{-14}	298		
$(3.12 \pm 0.58) \times 10^{-14}$	295 ± 2	Taketani et al., 2005	RR (g,h)
$(3.03 \pm 0.53) \times 10^{-14}$	295 ± 2	Taketani et al., 2005	RR (g,i)

Comments

(a) HO radicals were generated by the photolysis of H_2O at 185 nm in H_2O-CH_3CHF_2-C_2H_6-N_2-O_2 mixtures. The concentrations of CH_3CHF_2 and C_2H_6 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3CHF_2)/k(HO + C_2H_6) = 0.161 \pm 0.028$ is placed on an absolute basis by use of a rate coefficient of $k(HO + C_2H_6) = 2.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in H_2O (or O_3-H_2O)-CH_3CHF_2-CH_4-N_2-O_2 mixtures. The concentrations of CH_3CHF_2 and CH_4 were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(HO + CH_3CHF_2)/k(HO + CH_4) = 5.2 \pm 0.5$ (DeMore, 1992) and $k(HO + CH_3CHF_2)/k$(HO

+ CH_4) = (0.64 ± 0.13) exp[(599 ± 67)/T] (Hsu and DeMore, 1995) are placed on an absolute basis by use of a rate coefficient of k(HO + CH_4) = 1.85 × 10^{-20} $T^{2.82}$ exp(-987/T) cm^3 $molecule^{-1}$ s^{-1} (IUPAC, current recommendation).

(c) HO radicals were generated by the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or H_2O-O_3)-CH_3CHF_2-CH_3CCl_3-O_2-N_2 mixtures. The concentrations of CH_3CHF_2 and CH_3CCl_3 were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + CH_3CHF_2)/k(HO + CH_3CCl_3) = (1.53 ± 0.28) exp[(220 ± 57)/T] is placed on an absolute basis by use of a rate coefficient of k(HO + CH_3CCl_3) = 2.25 × 10^{-18} T^2 exp(-910/T) cm^3 $molecule^{-1}$ s^{-1} (IUPAC, current recommendation).

(d) Relative rate method. HO radicals were generated by photolyzing H_2O vapor at 185 nm. Reactant and reference compound concentrations were monitored by GC/MS.

(e) Relative to C_2H_6. An Arrhenius plot of the data gives the temperature dependence of the measured ratios as (0.17 ± 0.01) exp[-(58 ± 19)/T], which is placed on an absolute basis using a rate coefficient of k(HO + C_2H_6) = 1.49 × 10^{-17} T^2 exp(-499/T) cm^3 $molecule^{-1}$ s^{-1} (IUPAC, current recommendation).

(f) Relative to cyclopropane. An Arrhenius plot of the data gives the temperature dependence of the measured ratios as (0.29 ± 0.10) exp[(125 ± 42)/T]], which is placed on an absolute basis using a rate coefficient of k(HO + cyclo-C_3H_6) = 4.21 × 10^{-18} T^2 exp(-454/T) cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 2003).

(g) Relative rate method. HO radicals were generated by the UV photolysis of CH_3ONO in the presence of the reactant in 700 Torr total pressure of air diluent. Reference compound concentrations were monitored by FTIR. CH_3CHF_2 loss was measured indirectly from the observed formation of COF_2.

(h) Relative to C_2H_4. The measured rate coefficient ratio of k(CH_3CHF_2 + HO)/k(C_2H_4 + HO) = (3.59 ± 0.27) × 10^{-3} placed on an absolute basis by using a rate coefficient of k(C_2H_4 + HO) = 8.7 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 295 K (Calvert et al., 2000).

(i) Relative to C_2H_2. The measured rate coefficient ratio of k(CH_3CHF_2 + HO)/k(C_2H_2 + HO) = (3.58 ± 0.12) × 10^{-2} is placed on an absolute basis by using a rate coefficient of k(C_2H_2 + HO) = 8.45 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 296 K (Sørensen et al., 2003).

Preferred Values

k = 3.6 × 10^{-14} cm^3 $molecule^{-1}$ s^{-1} at 298 K.
k = 1.25 × 10^{-12} exp(-1070/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 210-300 K.

Reliability

$\Delta \log k = ^{+0.10}_{-0.20}$ at 298 K.
$\Delta (E/R) = ^{+200}_{-400}$ K.

Comments on Preferred Values

The absolute rate coefficients of Handwerk and Zellner (1978), Nip et al. (1979), Gierczak et al. (1991), and Kozlov et al. (2003) are in good agreement, and the relative rate coefficients of DeMore (1992) and Wilson et al. (2003) agree well with these absolute rate coefficients. The absolute rate coefficients of Clyne and Holt (1979) and Nielsen (1991) are systematically higher than the other absolute or relative rate coefficients, hence these data were not used in the evaluation. The data of Brown et al. (1990) are scattered and subject to large uncertainties, and those of Liu et al. (1990) exhibit a lower temperature dependence than the other absolute or relative rate coefficients - these studies were also not used in the evaluation. It is possible that the studies of Clyne and Holt (1979), Brown et al. (1990), Liu et al. (1990) and Nielsen (1991) were affected by reactant impurities. Of the data of Wilson et al. (2003), the rate data relative to C_2H_6 agrees very well with the absolute rate coefficients of Gierczak et al. (1991) and Kozlov et al. (2003). The Wilson et al. (2003) data relative to cyclopropane exhibits a lower temperature dependence compared with the data of Gierczak et al. (1991), Kozlov et al. (2003) and Wilson et al. (2003) relative to C_2H_6. This is attributed to uncertainties in the recommended rate constant for the cyclopropane reaction. Hence, only the Wilson et al. (2003) data relative to C_2H_6 were used in the evaluation. The relative rate coefficients of DeMore (1992) relative to C_2H_6 and CH_4 are in good agreement with each other, and in good agreement with the absolute rate coefficients of Howard and Evenson (1976), Handwerk and Zellner (1978), Nip et al. (1979), Gierczak et al. (1991), Kozlov et al. (2003), and the rate coefficients of Wilson et al. (2003) relative to C_2H_6. The relative rate coefficients of Hsu and DeMore (1995) are systematically lower and exhibit a slightly higher temperature dependence than the data of Gierczak et al. (1991), Kozlov et al. (2003), and Wilson et al. (2003) relative to C_2H_6.

The rate coefficient data of Howard and Evenson (1976), Handwerk and Zellner (1978), Nip et al. (1979), Gierczak et al. (1991) (using all data in the temperature range 212–422.5 K), DeMore (1992), Kozlov et al. (2003) and Wilson et al. (2003) (relative to C_2H_6) were fitted to a three parameter equation $k = CT^2$ exp(-D/T) giving $k = 2.80 \times 10^{-18}\ T^2$ exp(-580/T) over the temperature range 210–480 K. The preferred Arrhenius expression, $k = A$ exp(-B/T), is centered on a mid-range temperature, T_m, of 245 K and is derived from the three parameter equation with $A = C\ \mathrm{e}^2\ T_m^2$ and $B = D + 2T_m$. The relative rate data of Hsu and DeMore (1995) are approximately 16-18% lower than the preferred value at 298 K.

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IV.A1.16

$$\mathbf{HO + CH_3CF_3 \rightarrow H_2O + CH_2CF_3}$$

$\Delta H^\circ = -47.4\ \mathrm{kJ \cdot mol^{-1}}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.92 \pm 1.20) \times 10^{-11} \exp[-(3200 \pm 500)/T]$	333-425	Clyne and Holt, 1979	DF-RF (a)
$< 1.0 \times 10^{-15}$	293		
$(1.71 \pm 0.43) \times 10^{-15}$	298	Martin and Paraskevopoulos, 1983	FP-RA
$2.12 \times 10^{-12} \exp[-(2200 \pm 200)/T]$	261-374	Talukdar et al., 1991	DF-LMR/FP-LIF (b)
$(1.35 \pm 0.25) \times 10^{-15}$	298		
$9.51 \times 10^{-13} \exp[-(1979 \pm 65)/T]$	298-370	Orkin et al., 1996	FP-RF
$(1.24 \pm 0.09) \times 10^{-15}$	298		
Relative Rate Coefficients			
$7.96 \times 10^{-21}\, T^{2.82} \exp[-(1210 \pm 90)/T]$	298-403	Hsu and DeMore, 1995	RR (c,d)
1.30×10^{-15}	298		
$2.00 \times 10^{-18}\, T^2 \exp[-(1490 \pm 21)/T]$	298-383	Hsu and DeMore, 1995	RR (c,e)
1.20×10^{-15}	298		

Comments

(a) Although experiments were conducted over the temperature range 293–425 K, only an upper limit to the rate coefficient was obtained at 293 K.

(b) Kinetic data were obtained over the temperature range 223–374 K. Because the Arrhenius plot exhibited curvature below 261 K, the Arrhenius expression cited in the table was derived from the rate coefficients between 261–374 K.

(c) HO radicals generated by the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or O_3-H_2O)-CH_3CF_3-CH_4 (or CHF_2CF_3)-O_2-N_2 mixtures. The concentrations of CH_3CF_3 and CH_4 (or CHF_2CF_3) were measured by FTIR spectroscopy.

(d) The measured rate coefficient ratio $k(HO + CH_3CF_3)/k(HO + CH_4) = (0.43 \pm 0.12) \exp[-(223 \pm 90)/T]$ was placed on an absolute basis by use of the rate coefficient $k(HO + CH_4) = 1.85 \times 10^{-20}\, T^{2.82} \exp(-987/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(e) The measured rate coefficient ratio $k(HO + CH_3CF_3)/k(HO + CHF_2CF_3) = (2.16 \pm 0.14) \exp[-(370 \pm 21)/T]$ was placed on an absolute basis by use of the rate coefficient $k(HO + CHF_2CF_3) = 9.24 \times 10^{-19}\, T^2 \exp(-1120/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 9.2 \times 10^{-13} \exp(-1970/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The room temperature absolute rate coefficients of Martin and Paraskevopoulos (1983) and Talukdar et al. (1991) agree to within 20%, and taking into account the respective uncertainties in both studies, the agreement is reasonable. The rate coefficients of Hsu and DeMore, (1995) relative to the rate coefficients for the reactions of the HO radical with CH_4 and CHF_2CF_3, are in excellent agreement with each other. The rate coefficients of Orkin et al. (1996) are also in quite good agreement with the rate coefficients of Talukdar et al. (1991) and both sets of relative rate coefficients determined by Hsu and DeMore (1995). The rate coefficients of Clyne and Holt (1979) are not used in the evaluation because their rate coefficients at 333 K and 378 K are significantly higher than those of the other studies and have large associated uncertainties.

The rate coefficients of Martin and Paraskevopoulos (1983), Talukdar et al. (1991) (using their entire data set over the temperature range 223–374 K), Orkin et al. (1996), and Hsu and DeMore (1995) have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.91 \times 10^{-18} T^2 \exp(-1456/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 223–403 K. The preferred Arrhenius expression $k = A \exp(-B/T)$, is centered on a mid-range temperature, T_m, of 255 K and is derived from the three parameter equation with $A = C\, e^2\, T_m^2$ and $B = D + 2T_m$. The preferred values are 13% lower and 9% higher than the values of Talukdar et al. (1991) at 223 K and 261 K, respectively.

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IV.A1.17

$HO + CH_2FCH_2F \rightarrow H_2O + CH_2FCHF$

ΔH° = -69.5 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.12 \pm 0.12) \times 10^{-13}$	298	Martin and Paraskevopoulos, 1983	FP-RA
$5.11 \times 10^{-12} \exp[-(1190 \pm 106)/T]$	298-480	Kozlov et al., 2003	FP-RF
$1.02 \times 10^{-12} \exp[-(706 \pm 70)/T]$	210-298		
$(9.92 \pm 0.18) \times 10^{-14}$	298		
Relative Rate Coefficients			
$4.77 \times 10^{-18}\, T^2 \exp[-(454 \pm 23)/T]$	293-397	Wilson et al., 2003	RR (a,b)
9.23×10^{-14}	298		
$2.15 \times 10^{-18}\, T^2 \exp[-(188 \pm 29)/T]$	287-409	Wilson et al., 2003	RR (a,c)
1.20×10^{-13}	298		
$4.68 \times 10^{-18}\, T^2 \exp[-(441 \pm 16)/T]$	292-393	Wilson et al., 2003	RR (a,d)
9.46×10^{-14}	298		

Comments

(a) Relative rate method. HO radicals were generated by photolyzing H_2O vapor at 185 nm. Reactant and reference compound concentrations were monitored by GC/MS.

(b) Relative to C_2H_6. An Arrhenius plot of the data gives the temperature dependence of the measured ratios as $(0.32 \pm 0.02) \exp[(45 \pm 23)/T]$, which is placed on an absolute basis using a rate coefficient of $k(HO + C_2H_6) = 1.49 \times 10^{-17}\, T^2 \exp(-499/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) Relative to cyclopropane. An Arrhenius plot of the data gives the temperature dependence of the measured ratios as $(0.51 \pm 0.04) \exp[(266 \pm 29)/T]$], which is placed on an absolute basis using a rate coefficient of k(HO + cyclopropane) = $4.21 \times 10^{-18}\, T^2 \exp(-454/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

(d) Relative to CH_3CHF_2. An Arrhenius plot of the data gives the temperature dependence of the measured ratios as $(1.67 \pm 0.08) \exp[(139 \pm 16)/T]$, which is placed on an absolute basis using a rate coefficient of $k(HO + CH_3CHF_2) = 2.80 \times 10^{-18}\, T^2 \exp(-580/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.5 \times 10^{-12} \exp(-800/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210-300 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Kozlov et al. (2003) and the relative rate coefficients of Wilson et al. (2003) (relative to C_2H_6 and CH_2FCH_2F) are in good agreement over the temperature range 298–380 K. The absolute rate coefficient of Martin and Paraskevopoulos (1983) at 298 K agrees to within 20% or better to the data of Kozlov et al. (2003) and Wilson et al. (2003) (relative to C_2H_6 and CH_3CHF_2). The rate coefficients of Wilson et al. (2003) relative to cyclopropane exhibit a lower temperature dependence compared with the data of Kozlov et al. (2003) and the two other relative rate studies performed by Wilson et al. (2003). This may be due to the literature rate coefficient for HO + cyclopropane being not well established because of substantial scatter in the literature data. Therefore, the rate coefficients of Wilson et al. (2003) relative to cyclopropane were not used in the evaluation.

The absolute rate coefficients of Kozlov et al. (2003) and Martin and Paraskevopoulos (1983), and the relative rate coefficients of Wilson et al. (2003) relative to C_2H_6 and CH_3CHF_2 have been fitted to the three parameter equation $k = CT^2$ exp($-D/T$) resulting in $k = 3.39 \times 10^{-18}\ T^2$ exp($-312/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 210–480 K. The preferred Arrhenius expression, $k = A$ exp($-B/T$), is centered on a mid-range temperature, T_m, of 245 K and is derived from the three parameter equation with $A = C\ e^2\ T_m^2$ and $B = D + 2T_m$.

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IV.A1.18

$$\mathbf{HO + CH_2FCHF_2 \rightarrow H_2O + CH_2FCF_2} \quad (1)$$
$$\mathbf{\rightarrow H_2O + CHFCHF_2} \quad (2)$$

$\Delta H°(1)$ = -78.0 kJ·mol^{-1}
$\Delta H°(2)$ = -80.1 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.48×10^{-12} exp[-(1000 ± 100)/T]	293-425	Clyne and Holt, 1979	DF-RF
$(4.68 \pm 0.40) \times 10^{-14}$	294		
$(1.83 \pm 0.18) \times 10^{-14}$	298	Martin and Paraskevopoulos, 1983	FP-RA
Relative Rate Coefficients			
4.97×10^{-18} T^2 exp(-1012/T)	278-323	Barry et al., 1995	RR (a)
$(1.49 \pm 0.05) \times 10^{-14}$	298 ± 2		

Comments

(a) HO radicals were generated by the photolysis of O_3 in the presence of water vapor at ∼250 nm at atmospheric pressure of air. Irradiations of O_3-H_2O-CH_2FCHF_2-CH_3CCl_3-air mixtures were carried out and the concentrations of CH_2FCHF_2 and CH_3CCl_3 measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of k(HO + CH_2FCHF_2)/k(HO + CH_3CCl_3) = 2.21 exp(-102/T) is placed on an absolute basis by use of a rate coefficient of k(HO + CH_3CCl_3) = 2.25×10^{-18} T^2 exp(-910/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.3 \times 10^{-12}$ exp(-1610/T) cm^3 molecule^{-1} s^{-1} over the temperature range 270-330 K.

Reliability

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

Comments on Preferred Values

The rate coefficient of Martin and Paraskevopoulos (1983) at 298 K is ∼25% higher than the 298 K value Barry et al. (1995). The preferred rate coefficients are therefore derived from the relative rate study of Barry et al. (1995). The preferred Arrhenius expression, $k = A$ exp($-B/T$), is derived from the three parameter expression cited in the table ($k = 4.97 \times 10^{-18}$ T^2 exp(-1012/T) cm^3 molecule^{-1} s^{-1} over the temperature range 278–323 K) and is centered on a mid-range temperature, T_m, of 300 K with $A = C$ e^2 T_m^2 and $B = D + 2T_m$.

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IV.A1.19

$HO + CH_2FCF_3 \rightarrow H_2O + CHFCF_3$

$\Delta H° = -63.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$3.2 \times 10^{-12} \exp[-(1800 \pm 200)/T]$	294-429	Clyne and Holt, 1979	DF-RF
$(5.5 \pm 0.7) \times 10^{-15}$	294		
$(5.2 \pm 0.6) \times 10^{-15}$	298	Martin and Paraskevopoulos, 1983	FP-RA
$1.1 \times 10^{-12} \exp[-(1424 \pm 35)/T]$	249-473	Jeong et al., 1984	DF-RF
$(8.44 \pm 0.73) \times 10^{-15}$	298		
$5.8 \times 10^{-12} \exp[-(1350)/T]$	231-423	Brown et al., 1990	DF-RF
6.25×10^{-15}	298		
$3.7 \times 10^{-12} \exp[-(1990 \pm 280)/T]$	270-400	Liu et al., 1990	FP-RF
$(5.18 \pm 0.70) \times 10^{-15}$	298		
$5.7 \times 10^{-13} \exp[-(1430 \pm 60)/T]$	223-324	Gierczak et al., 1991	DF-LMR/FP-LIF (a)
$(4.34 \pm 0.35) \times 10^{-15}$	298		
$(2.38 \pm 0.22) \times 10^{-15}$	270	Zhang et al., 1992	DF-RF
$1.03 \times 10^{-12} \exp[-(1588 \pm 52)/T]$	298-460	Orkin and Khamaganov, 1993	DF-EPR
$(5.00 \pm 0.44) \times 10^{-15}$	298		
$9.9 \times 10^{-13} \exp[-(1640 \pm 150)/T]$	255-424	Leu and Lee, 1994	DF-RF
$(3.9 \pm 0.6) \times 10^{-15}$	298		
$(4.6 \pm 0.5) \times 10^{-15}$	295	Bednarek et al., 1996	LP-UVA
Relative Rate Coefficients			
$8.26 \times 10^{-21}\, T^{2.82} \exp[-(905 \pm 115)/T]$	298-358	DeMore, 1993	RR (b,c)
3.76×10^{-15}	298		
$1.84 \times 10^{-18}\, T^{2} \exp[-(1129 \pm 44)/T]$	298-358	DeMore, 1993	RR (b,d)
3.70×10^{-15}	298		
$1.93 \times 10^{-18}\, T^{2} \exp[-(1132 \pm 79)/T]$	298-358	DeMore, 1993	RR (b,e)
3.84×10^{-15}	298		
$(3.90 \pm 0.48) \times 10^{-15}$	298 ± 2	Barry et al., 1995	RR (f)
$(4.19 \pm 0.19) \times 10^{-15}$	298 ± 2	Barry et al., 1995	RR (g)

Comments

(a) Measurements were performed up to a temperature of 450 K. The Arrhenius expression only covers the temperature range 223–324 K to avoid curvature in the Arrhenius plot.

(b) Relative rate method. HO radicals were generated by the irradiation of O_3-H_2O-O_2-Ar mixtures at 254 nm. The CH_2FCF_3, CH_4, CH_3CCl_3, and CHF_2CF_3 concentrations were monitored during the experiments by FTIR absorption spectroscopy. The measured rate coefficient ratios of $k(HO + CH_4)/k(HO + CH_2FCF_3) = (2.24 \pm 0.78) \exp[-(82 \pm 115)/T]$, $k(HO + CH_3CCl_3)/k(HO + CH_2FCF_3) = (1.22 \pm 0.17) \exp[(219 \pm 44)/T]$ and $k(HO + CHF_2CF_3/k(HO + CH_2FCF_3) = (0.48 \pm 0.12) \exp[(12 \pm 79)/T]$ are placed on an absolute basis by use of rate coefficients $k(HO + CH_4) = 1.85 \times 10^{-20}\, T^{2.82} \exp(-987/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation), $k(HO + CH_3CCl_3) = 2.25 \times 10^{-18}\, T^2 \exp(-910/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation) and $k(HO + CHF_2CF_3) = 9.24 \times 10^{-19}\, T^2 \exp(-1120/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) Relative to $k(HO + CH_4)$.

(d) Relative to $k(\mathrm{HO} + \mathrm{CH_3CCl_3})$.

(e) Relative to$k(\mathrm{HO} + \mathrm{CHF_2CF_3})$.

(f) Relative rate method. HO radicals were generated by the photolysis of O_3 at ~250 nm in the presence of water vapor at atmospheric pressure of air. Irradiations of O_3-H_2O-CH_2FCF_3-CH_3CCl_3-air mixtures were carried out at 298 ± 2 K and the concentrations of CH_2FCF_3 and CH_3CCl_3 measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of $k(\mathrm{HO} + \mathrm{CH_2FCF_3})/k(\mathrm{HO} + \mathrm{CH_3CCl_3}) = 0.41 \pm 0.05$ is placed on an absolute basis by using a rate coefficient of $k(\mathrm{HO} + \mathrm{CH_3CCl_3}) = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(g) Relative rate method. HO radicals were generated by the photolysis of O_3 in the presence of water vapor. Irradiations of O_3-H_2O-CH_2FCF_3-CH_2FCHF_2-air mixtures were carried out at 298 ± 2 K and the concentrations of CH_2FCF_3 and CH_2FCHF_2 measured by GC and FTIR spectroscopy. The measured rate coefficient ratio $k(\mathrm{HO} + \mathrm{CH_2FCHF_2})/k(\mathrm{HO} + \mathrm{CH_2FCF_3}) = 3.58 \pm 0.16$ is placed on an absolute basis by using a rate coefficient of $k(\mathrm{HO} + \mathrm{CH_2FCHF_2}) = 1.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

Preferred Values

$k = 4.6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.9 \times 10^{-13} \exp(-1395/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-300 K.

Reliability

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

Comments on Preferred Values

The absolute rate coefficient of Zhang et al. (1992) at 270 K is in good agreement with those of Liu et al. (1990), Gierczak et al. (1991) and Leu and Lee (1994) over the temperature range 270–273 K. The absolute rate coefficients of Orkin and Khamaganov (1993) are in agreement with those of Gierczak et al. (1991) and Leu and Lee (1994). At 298 K, the relative rate coefficients of DeMore (1993) and Barry et al. (1995) are lower than the absolute rate coefficients of Martin and Paraskevopoulos (1983), Liu et al. (1990), Gierczak et al. (1991) and Orkin and Khamaganov (1993) by up to 30%. On the other hand, the absolute rate coefficients of Leu and Lee (1994) are in good agreement with the relative rate coefficients of DeMore (1993) and Barry et al. (1995), and are between 10-20% lower than the absolute rate coefficients of Gierczak et al. (1991) and Orkin and Khamaganov (1993). Above 298 K, the absolute rate coefficients of Liu (1990) are up to 30% higher than those of Gierczak et al. (1991). The high rate coefficients of Clyne and Holt (1979), Brown et al. (1990) and Jeong et al. (1984) were not used in the evaluation.

The absolute rate coefficients of Martin and Paraskevopoulos (1983), Liu et al. (1990), Gierczak et al. (1991), Zhang et al. (1992), Orkin and Khamaganov (1993), Leu and Lee (1994), Bednarek et al. (1996), and the relative rate coefficients of Barry et al. (1995) have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, giving $k = 1.0 \times 10^{-18}\ T^2 \exp(-885/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–460 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered on a mid-range temperature, T_m, of 255 K and is derived from the three parameter equation with $A = C\ \mathrm{e}^2\ T_m^2$ and $B = D + 2T_m$. This expression yields rate coefficients that are 10-15% higher than those calculated from the rate coefficient expressions tabulated for DeMore (1993).

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IV.A1.20

$HO + CHF_2CHF_2 \rightarrow H_2O + CF_2CHF_2$

ΔH° = -58.41 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.76×10^{-12} exp[-(1800 ± 400)/T]	294-434	Clyne and Holt, 1979	DF-RF
6.57×10^{-15}	298		
Relative Rate Coefficients			
2.67×10^{-18} T^2 exp[-(1122 ± 37)/T]	298-358	DeMore, 1993	RR (a)
5.50×10^{-15}	298		
1.18×10^{-18} T^2 exp[-(805 ± 25)/T]	298-358	DeMore, 1993	RR (b)
7.0×10^{-15}	298		
1.93×10^{-18} T^2 exp[-(1011 ± 77)/T]	298-358	DeMore, 1993	RR (c)
5.76×10^{-15}	298		

Comments

(a) HO radicals were generated by the photolysis of O_3-H_2O-O_2-Ar mixtures at 254 nm. The concentrations of CHF_2CHF_2 and CH_3CCl_3 were measured during the experiments by FTIR absorption spectroscopy. The measured rate coefficient ratio of k(HO + CH_3CCl_3)/k(HO + CHF_2CHF_2) = (0.84 ± 0.10) exp[(212 ± 37)/T] is placed on an absolute basis by use of a rate coefficient of k(HO + CH_3CCl_3) = 2.25×10^{-18} T^2 exp(-910/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of O_3-H_2O-O_2-Ar mixtures at 254 nm. The concentrations of CHF_2CHF_2 and CH_2FCF_3 were measured during the irradiations by FTIR absorption spectroscopy. The measured rate coefficient ratio of k(HO + CH_2FCF_3)/(k(HO + CHF_2CHF_2) = (0.85 ± 0.07) exp[-(80 ± 25)/T] is placed on an absolute basis by use of the rate coefficient k(HO + CH_2FCF_3) = 1.0×10^{-18} T^2 exp(-885/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) HO radicals were generated by irradiation of O_3-H_2O-O_2-Ar mixtures at 254 nm. The concentrations of CHF_2CHF_2 and CHF_2CF_3 were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of k(HO + CHF_2CF_3)/k(HO + CHF_2CHF_2) = (0.48 ± 0.11) exp[-(109 ± 77)/T] is placed on an absolute basis by use of the rate coefficient k(HO + CHF_2CF_3) = 9.24×10^{-19} T^2 exp(-1120/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 6.1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.4 \times 10^{-12}$ exp(-1620/T) cm^3 molecule^{-1} s^{-1} over the temperature range 290-360 K.

Reliability

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

Comments on Preferred Values

The relative rate coefficients of DeMore (1993) using three reference compounds are in good agreement (within 20% over the temperature range 298–358 K). While the 298 K rate coefficient of Clyne and Holt (1979) is also in good agreement with the relative rate coefficients of DeMore (1993), the temperature dependence reported by Clyne and Holt (1979) is significantly higher than those of DeMore (1993). The data of Clyne and Holt (1979) is also sparse and scattered. Therefore the data of Clyne and Holt (1979) are not used in the evaluation.

The preferred 298 K rate coefficient is an average of the three relative rate measurements of DeMore (1993). The relative rate coefficients of DeMore (1993) were placed on an absolute basis and fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.80 \times 10^{-18}\ T^2 \exp(-974/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–360 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$ is centered on a mid-range temperature, T_m, of 320 K and is derived from the three parameter equation with $A = C\ e^2\ T_m^2$ and $B = D + 2T_m$.

References

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DeMore, W. B.: Geophys. Res. Lett. 20, 1359, 1993.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.

IV.A1.21

$$\mathbf{HO + CHF_2CF_3 \rightarrow H_2O + CF_2CF_3}$$

ΔH° = -54.1 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.70×10^{-13} exp[-(1100 ± 100)/T]	294-441	Clyne and Holt, 1979	DF-RF
(4.9 ± 1.4) × 10^{-15}	294		
(2.49 ± 0.27) × 10^{-15}	298	Martin and Paraskevopoulos, 1983	FP-RA
2.8×10^{-13} exp[-(1350 ± 100)/T]	257-423	Brown et al., 1990	DF-RF
(2.69 ± 0.93) × 10^{-15}	298		
5.41×10^{-13} exp[-(1700 ± 100)/T]	220-364	Talukdar et al., 1991	DF-LMR/PLP-LIF
(1.90 ± 0.27) × 10^{-15}	298		
Relative Rate Coefficients			
(1.64 ± 0.21) × 10^{-15}	298	DeMore, 1992	RR (a)

Comments

(a) HO radicals were generated by the photolysis of O_3 in the presence of water vapor at 254 nm. Irradiations of O_3-H_2O-CHF_2CF_3-CH_4-O_2-N_2 (or Ar) mixtures were carried out, and the concentrations of CHF_2CF_3 and the CH_4 were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio k(HO + CH_4)/k(HO + CF_3CHF_2) = 3.9 ± 0.50 is placed on an absolute basis by use of the rate coefficient k(HO + CH_4) = 6.4 × 10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

Preferred Values

k = 1.9 × 10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 4.4 × 10^{-13} exp(-1630/T) cm^3 molecule^{-1} s^{-1} over the temperature range 220–300 K.

Reliability

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

Comments on Preferred Values

The relatively high results of Clyne and Holt (1979) and Brown et al. (1990) suggest the presence of reactive impurities in the CHF_2CF_3 samples used in their studies. These data were therefore not used in the evaluation. At 298 K, the rate coefficients of DeMore (1992) and Talukdar et al. (1991) agree to within 10%; the rate coefficient of Martin and Paraskevopoulos (1983) is 30% higher than the corresponding value of Talukdar et al. (1991). The rate coefficient data of Martin and Paraskevopoulos (1983), Talukdar et al. (1991) and DeMore (1992) were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 9.24 \times 10^{-19}\ T^2 \exp(-1120/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–360 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered on a mid-range temperature, T_m, of 255 K and is derived from the three parameter equation with $A = C\ e^2\ T_m^2$ and $B = D + 2T_m$.

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IV.A1.22

$$\begin{aligned} \mathbf{HO + CHF_2CF_2CH_2F} &\rightarrow \mathbf{H_2O + CHF_2CF_2CHF} \quad (1)\\ &\rightarrow \mathbf{H_2O + CF_2CF_2CH_2F} \quad (2) \end{aligned}$$

Rate coefficient data(k = k_1 + k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.87×10^{-12} exp[-(1661 ± 170)/T]	260-365	Zhang et al., 1994	FP-RF
(1.09 ± 0.03) × 10^{-14}	298		
Relative Rate Coefficients			
1.24×10^{-20} $T^{2.82}$ exp[-(823 ± 34)/T]	286-364	Hsu and DeMore, 1995	RR (a)
7.44×10^{-15}	298		

Comments

(a) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or H_2O-O_3)-$CHF_2CF_2CH_2F$-CH_4-O_2-N_2 mixtures. The concentrations of $CHF_2CF_2CH_2F$ and CH_4 were measured by FTIR absorption spectroscopy. The measured rate coefficient of k(HO + $CHF_2CF_2CH_2F$)/k(HO + CH_4) = (0.67 ± 0.07) exp[(164 ± 34)/T] is placed on an absolute basis by use of a rate coefficient of k(HO + CH_4) = 1.85 × 10^{-20} $T^{2.82}$ exp(-987/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

k = 7.7 × 10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 2.2 × 10^{-12} exp(-1685/T) cm^3 molecule^{-1} s^{-1} over the temperature range 285-365 K.

Reliability

Δ log k = ± 0.3 at 298 K.
Δ (E/R) = ± 300 K.

Comments on Preferred Values

The relative rate coefficients of Hsu and DeMore (1995) are uniformly a factor of 1.5 lower than the absolute rate coefficients of Zhang et al. (1994) over the temperature range common to both studies (286–364 K). This suggests the presence of reactive impurities or of secondary reactions in the study of Zhang et al. (1994). The relative rate coefficients of Hsu and DeMore (1995) were used to derive the preferred values. These data were fitted to the three parameter equation, $k = CT^2$ exp(-D/T), resulting in k = 2.84 × 10^{-18} T^2 exp(-1045/T) cm^3 molecule^{-1} s^{-1} over the temperature range 285–365 K. The preferred Arrhenius expression, $k = A$ exp(B/T), is centered on a mid-range temperature, T_m, of 320 K and is derived from the three parameter equation with $A = C$ e^2 T_m^2 and $B = D + 2T_m$.

References

Hsu, K.-J. and DeMore, W. B.: J. Phys. Chem. 99, 1235, 1995.
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Zhang, Z., Padmaja, S., Saini, R. D., Huie, R. E. and Kurylo, M. J.: J. Phys. Chem. 98, 4312, 1994.

IV.A1.23

$HO + CF_3CF_2CH_2F \rightarrow H_2O + CF_3CF_2CHF$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.6 \times 10^{-13} \exp[-(1107 \pm 202)/T]$	256-314	Garland et al., 1993	PLP-LIF
$(6.4 \pm 0.6) \times 10^{-15}$	295		

Preferred Values

$k = 6.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.6 \times 10^{-13} \exp(-1100/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-320 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred values are derived from the sole study of Garland et al. (1993).

References

Garland, N. L., Medhurst, L. J. and Nelson, H. H.: J. Geophys. Res. 98, 23107, 1993.

IV.A1.24

$$\mathbf{HO + CF_3CHFCHF_2 \rightarrow H_2O + CF_3CFCHF_2} \quad (1)$$
$$\mathbf{\rightarrow H_2O + CF_3CHFCF_2} \quad (2)$$

Rate coefficient data(k = k_1 + k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.0×10^{-13} exp[-(1007 ± 151)/T]	251-311	Garland et al., 1993	PLP-LIF
(6.5 ± 0.5) × 10^{-15}	294		
1.05×10^{-12} exp[-(1434 ± 161)/T]	260-365	Zhang et al., 1994	FP-RF
(8.51 ± 0.26) × 10^{-15}	298		
(4.93 ± 0.25) × 10^{-15}	294	Nelson et al., 1995	DF-LIF
Relative Rate Coefficients			
6.7×10^{-21} $T^{2.82}$ exp[-(756 ± 12)/T]	298-380	Hsu and DeMore, 1995	RR (a)
5.0×10^{-15}	298		

Comments

(a) HO radicals were generated by the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV, in H_2O (or O_3-H_2O)-$CF_3CHFCHF_2$-CH_4-O_2-N_2 mixtures. The concentrations of $CF_3CHFCHF_2$ and CH_4 were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of k(HO + $CF_3CHFCHF_2$)/k(HO + CH_4) = (0.36 ± 0.01) exp[(231 ± 12)/T] is placed on an absolute basis by using a rate coefficient of k(HO + CH_4) = 1.85×10^{-20} $T^{2.82}$ exp(-987/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

k = 5.0×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 1.4×10^{-12} exp(-1680/T) cm^3 molecule^{-1} s^{-1} over the temperature range 290-380 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are derived from the relative rate coefficients of Hsu and DeMore (1995) and the absolute rate study by Nelson et al. (1995). These data were fitted to the three parameter equation, $k = CT^2$ exp(-D/T), resulting in k = 1.76×10^{-18} T^2 exp(-1021/T) cm^3 molecule^{-1} s^{-1} over the temperature range 294–380 K. The preferred Arrhenius expression, k = A exp(-B/T), is centered on a mid-range temperature, T_m, of 330 K and is derived from the three parameter equation, $k = A$ exp(-B/T) with $A = Ce^2\ T_m^2$ and $B = D + 2T_m$. The higher values of Garland et al. (1993) and Zhang et al. (1994) were not used in this evaluation as their experiments may have been subject to problems arising from the presence of impurities.

References

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IV.A1.25

$HO + CF_3CH_2CF_3 \rightarrow H_2O + CF_3CHCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.0 \times 10^{-14} \exp[-(906 \pm 151)/T]$	257-311	Garland et al., 1993	PLP-LIF
9.6×10^{-16}	298		
$(5.1 \pm 0.7) \times 10^{-16}$	294	Nelson et al., 1995	DF-LIF
$(4.15 \pm 0.33) \times 10^{-16}$	298	Garland and Nelson, 1996	PLP-LIF
$(1.6 \pm 0.4) \times 10^{-12} \exp[-(2540 \pm 150)/T]$	273-413	Gierczak et al., 1996	FP-LIF
$(3.20 \pm 0.60) \times 10^{-16}$	298		
Relative Rate Coefficients			
$1.16 \times 10^{-18}\, T^2 \exp[-(1700 \pm 109)/T]$	298-367	Hsu and DeMore, 1995	RR (a)
3.43×10^{-16}	298		
$(3.5 \pm 1.5) \times 10^{-16}$	298	Barry et al., 1997	RR (b)

Comments

(a) Relative rate method. HO radicals were generated from the photolysis of H_2O at 185 nm or of O_3-H_2O mixtures in the UV in H_2O (or O_3-H_2O)-$CF_3CH_2CF_3$-CHF_2CF_3-O_2-N_2 mixtures. The concentrations of $CF_3CH_2CF_3$ and CHF_2CF_3 were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(HO + CF_3CH_2CF_3)/k(HO + CHF_2CF_3) = (1.26 \pm 0.41) \exp[-(580 \pm 109)/T]$ is placed on an absolute basis by using a rate coefficient of $k(HO + CHF_2CF_3) = 9.24 \times 10^{-19}\, T^2 \exp(-1120/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) Relative rate method. HO radicals were generated by UV photolysis of O_3 at 254 nm in the presence of H_2O vapour. Mixtures of $O_3/CF_3CH_2CF_3/CF_3CH_2CF_2CH_3/H_2O$ were photolysed in air at 298 K, $k(HO + CF_3CH_2CF_3)/k(HO + CF_3CH_2CF_2CH_3)$ was found to be 0.06 ± 0.02. Using the experimentally derived value of $k(HO + CF_3CH_2CF_2CH_3) = 2.0 \times 10^{-12} \exp[-(1750 \pm 400)/T]$ cm^3 molecule^{-1} s^{-1} gives $k(HO + CF_3CH_2CF_3) = (3.5 \pm 1.5) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k = 3.3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.3 \times 10^{-12} \exp(-2465/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–340 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred values are derived from the relative rate coefficients of Hsu and DeMore (1995) and the absolute rate coefficients of Gierczak et al. (1996). The agreement between the data of Hsu and DeMore (1995), when placed on an absolute basis as described above, and the data of Gierczak et al. (1996) is very good over the temperature range 298-367 K. The absolute rate coefficients of Garland et al. (1993) over the temperature range 257-311 K are consistently higher than those of Hsu and

DeMore (1995) and Gierczak et al. (1996) and were not used in the evaluation. The absolute rate coefficient of Nelson et al. (1995) is also relatively large and has a large uncertainty; this value was also not used in the evaluation.

The data of Hsu and DeMore (1995) and Gierczak et al. (1996) were fitted to the three parameter equation, $k = CT^2$ exp(-D/T), resulting in k = 1.91 × 10^{-18} T^2 exp(-1865/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 273–413 K. The preferred Arrhenius expression, $k = A$ exp(-B/T), is centered on a mid-range temperature, T_m, of 300 K and is derived from the three-parameter equation with $A = Ce^2\ T_m^2$ and $B = D + 2T_m$. Note that the preferred Arrhenius expression should not be used outside the specified temperature range (270–340 K); rather, the full three parameter expression should be used.

The relative rate study of Barry et al. (1997) at 298 K is in very good agreement with the recommended value. However, the very small rate constant ratio would lead to large uncertainties, therefore the rate coefficient derived by Barry et al. (1997) was not used in the evaluation. The preferred value at 298 K is 30% lower than the absolute rate coefficient of Garland and Nelson (1996), but taking into account the uncertainty in the Garland and Nelson (1996) value, the agreement is reasonable.

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IV.A1.26

$$\mathbf{HO + CF_3CHFCF_3 \rightarrow H_2O + CF_3CFCF_3}$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
3.7×10^{-13} exp[-(1615 ± 190)/T]	294-369	Nelson et al., 1993	DF-LIF
(1.64 ± 0.28) × 10^{-15}	295		
3.8×10^{-13} exp[-(1596 ± 77)/T]	298-463	Zellner et al., 1994	PLP-LIF
(1.8 ± 0.2) × 10^{-15}	298		
3.63×10^{-13} exp[-(1613 ± 135)/T]	270-365	Zhang et al., 1994	FP-RF
(1.62 ± 0.03) × 10^{-15}	298		
6.19×10^{-13} exp[-(1830 ± 100)/T]	250-430	Tokuhashi et al., 2004	FP/PLP-LIF (a)
(1.34 ± 0.08) × 10^{-15}	298		
Relative Rate Coefficients			
3.15×10^{-21} $T^{2.82}$ exp[-(870 ± 105)/T]	296-398	Hsu and DeMore, 1995	RR (b,c)
1.55×10^{-15}	296		
7.67×10^{-19} T^2 exp[-(1082 ± 89)/T]	298-367	Hsu and DeMore, 1995	RR (b,d)
1.80×10^{-15}	298		

Comments

(a) HO radical concentration monitored by laser induced fluorescence.

(b) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or O_3 at 254 nm, in H_2O (or O_3-H_2O) - CF_3CHFCF_3 - CH_4 (or CHF_2CF_3)- O_2 - N_2 mixtures. The concentrations of CF_3CHFCF_3 and CH_4 (or CHF_2CF_3) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratios of k(HO + CF_3CHFCF_3)/k(HO + CH_4) = (0.17 ± 0.05) exp[(117 ± 105)/T] and k(HO + CF_3CHFCF_3)/ k(HO + CHF_2CF_3) = (0.83 ± 0.22) exp[(38 ± 89)/T] are placed on an absolute basis by use of rate coefficients of k(HO + CH_4) = 1.85×10^{-20} $T^{2.82}$ exp(-987/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation) and k(HO + CHF_2CF_3) = 9.24×10^{-19} T^2 exp(-1120/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) Relative to k(HO + CH_4).

(d) Relative to k(HO + CHF_2CF_3).

Preferred Values

$k = 1.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.3 \times 10^{-13}$ exp(-1770/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250-380 K.

Reliability

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

Comments on Preferred Values

The preferred values are derived from absolute rate coefficients of Zhang et al. (1994) and Tokuhashi et al. (2004). The relative rate coefficients of Hsu and DeMore (1995), and the absolute rate coefficients of Nelson et al. (1993) and Zellner et al. (1994) are 10-30% higher than those of Tokuhashi et al. (2004) over the temperature range 298–380 K, with the agreement being better at the higher temperatures. Tokuhashi et al. (2004) used highly purified reactants in their study, suggesting that the previous studies may have been affected by reactant impurities.

The data of Zellner et al. (1994), Zhang et al. (1994) and Tokuhashi et al. (2004) were fitted to the three parameter equation, $k = CT^2$ exp(-D/T), resulting in $k = 8.0 \times 10^{-19}\ T^2$ exp(-1170/T) $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ over the temperature range 250–430 K. The preferred Arrhenius expression, $k = A$ exp(-B/T), is centered on a mid-range temperature, T_m, of 300 K and is derived from the three parameter equation with $A = Ce^2\ T_m^2$ and $B = D + 2T_m$. Note that the preferred Arrhenius expression should not be used outside the specified temperature range (250–380 K); rather, the full three parameter expression should be used.

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IV.A1.27

$HO + CHF_2OCHF_2 \rightarrow H_2O + CHF_2OCF_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.47 \pm 0.2) \times 10^{-14}$	296	Zhang et al., 1992	FP-RF
$5.4 \times 10^{-13} \exp[-(1560 \pm 200)/T]$	269-312	Garland et al., 1993	LP-LIF
$(3.0 \pm 0.7) \times 10^{-15}$	295		
$6.3 \times 10^{-13} \exp[-(1646 \pm 76)/T]$	277-370	Orkin et al., 1999	FP-RF
$(2.52 \pm 0.17) \times 10^{-15}$	298		
Relative Rate Coefficients			
$2.36 \times 10^{-18}\, T^2 \exp[-(1366 \pm 62)/T]$	298-368	Hsu and DeMore, 1995	RR (a)
2.1×10^{-15}	298		
$2.12 \times 10^{-18}\, T^2 \exp[-(1313 \pm 10)/T]$	273-465	Wilson et al., 2001	RR (b)
2.29×10^{-15}	298		

Comments

(a) HO radicals were generated from the photolysis of H_2O at 185 nm or O_3 at 254 nm in the presence of H_2O. The concentrations of CHF_2OCHF_2 and CH_3CCl_3 were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(HO + CHF_2OCHF_2)/k(HO + CH_3CCl_3) = (1.05 \pm 0.20) \exp[-(456 \pm 62)/T]$ is placed on an absolute basis by using the rate coefficient for $k(HO + CH_3CCl_3) = 2.25 \times 10^{-18}\, T^2 \exp(-910/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) HO radicals were generated from the photolysis of H_2O vapour in the reaction mixture at 185 nm. The concentrations of CHF_2OCHF_2 and CF_3CHF_2 were monitored by GCMS. An Arrhenius plot of the Wilson et al. (2001) data gives a rate coefficient ratio of $k(HO + CHF_2OCHF_2)/k(HO + CF_3CHF_2) = (2.29 \pm 0.06) \exp[-(193 \pm 10)/T]$ over the temperature range 273–465 K. The rate coefficient ratio was placed on an absolute basis by using a rate coefficient of $k(HO + CHF_2CF_3) = 9.24 \times 10^{-19}\, T^2 \exp(-1120/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation)

Preferred Values

$k = 2.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.9 \times 10^{-12} \exp(-2020/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270-460 K.

Reliability

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

Comments on Preferred Values

The absolute rate coefficients of Orkin et al. (1999) and the relative rate coefficients of Hsu and DeMore (1995) and Wilson et al. (2001) are in good agreement over the temperature range 273–370 K. The 296 K rate coefficient of Zhang et al. (1992) is an order of magnitude higher than all other values, presumably due to the presence of impurities in their CHF_2OCHF_2 samples. The measurements of Garland et al. (1993) are scattered. Thus, neither the data of Zhang et al. (1992) nor the data of Garland et al. (1993) were used in the evaluation.

The preferred values were obtained from the rate coefficient data of Hsu and DeMore (1995), Orkin et al. (1999) and Wilson et al. (2001). These rate coefficient data were fitted to the three-parameter equation k = CT^2 exp(-D/T), resulting in k = 2.22 × 10^{-18} T^2 exp(-1338/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 273–464 K. The preferred Arrhenius expression, k = A exp(-B/T), is centered on a mid-range temperature, T_m, of 340 K with $A = Ce^2\ T_m^2$ and $B = D + 2T_m$.

Good et al. (1999) have performed experiments and ab initio calculations to determine the mechanism of CHF_2OCHF_2 oxidation under atmospheric conditions (no kinetic data was reported). Activation barriers were calculated for various steps, and an oxidation mechanism was described.

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IV.A1.28

$HO + HC(O)F \rightarrow H_2O + FCO$

ΔH° = -56.2 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$< 5.0 \times 10^{-15}$	296 ± 2	Wallington and Hurley, 1993	RR (a)

Comments

(a) HO radicals were generated from the photolysis of O_3-H_2-O_2 mixtures, and HC(O)F was formed in situ from the oxidation of CH_3F. No losses of HC(O)F were observed, leading to a rate coefficient ratio of $k(HO + HC(O)F)/k(HO + CH_3F) < 0.25$. This upper limit to the rate coefficient ratio is placed on an absolute basis by use of $k(HO + CH_3F) = 2.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k < 1.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is derived from the sole study of Wallington and Hurley (1993), with the higher upper limit reflecting uncertainties in the reference reaction rate coefficient.

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IV.A1.29

$$\begin{aligned} \mathbf{HO + CHF_2CHO} &\rightarrow \mathbf{H_2O + CHF_2CO} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{H_2O + CF_2CHO} \quad \mathbf{(2)} \end{aligned}$$

$\Delta H°(1) = -110.4\ \mathrm{kJ \cdot mol^{-1}}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.7 \pm 0.2) \times 10^{-12}$	298 ± 2	Scollard et al., 1993	PLP-RF
Relative Rate Coefficients			
$(1.3 \pm 0.3) \times 10^{-12}$	298 ± 2	Scollard et al., 1993	RR (a)
$(1.8 \pm 0.4) \times 10^{-12}$	298 ± 2	Sellevåg et al., 2005	RR (b)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO (or C_2H_5ONO)-NO-CHF_2CHO-toluene-air mixtures at 1 bar pressure. The concentrations of CHF_2CHO and toluene were measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of k(HO + CHF_2CHO)/k(HO + toluene) is placed on an absolute basis by using a rate coefficient of k(HO + toluene) = 5.63×10^{-12} cm^3 molecule^{-1} s^{-1} (Calvert et al., 2002).

(b) HO radicals were generated by the photolysis of O_3 in the presence of H_2-CHF_2CHO-propane-air mixtures at 1 bar pressure. The concentrations of CHF_2CHO and propane were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + CHF_2CHO)/k(HO + C_3H_8) = 1.62 ± 0.04 is placed on an absolute basis by using a rate coefficient of k(HO + C_3H_8) = 1.1×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation)

Preferred Values

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

Reliability

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

Comments on Preferred Values

The absolute and relative rate coefficients of Scollard et al. (1993) and Sellevåg et al. (2005) are in good agreement, and the preferred value is the average of these rate coefficients. The reaction is expected to proceed by pathway (1) (Scollard et al., 1993), which is supported by the quantum chemical calculations of Sellevåg et al. (2005).

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IV.A1.30

$HO + CF_3CHO \rightarrow H_2O + CF_3CO$

ΔH° = -107.2 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.1 \pm 0.7) \times 10^{-12}$	299 ± 3	Dóbé et al., 1989	DF-RF
$(6.5 \pm 0.5) \times 10^{-13}$	298 ± 2	Scollard et al. 1993	PLP-RF
Relative Rate Coefficients			
$(4.4 \pm 1.0) \times 10^{-13}$	298 ± 2	Scollard et al. 1993	RR (a)
$(4.8 \pm 0.3) \times 10^{-13}$	298 ± 2	Sellevåg et al. 2004	RR (b)
$(6.15 \pm 0.80) \times 10^{-13}$	296 ± 2	Sulbaek Anderson et al., 2004	RR (c,d)
$(6.93 \pm 0.81) \times 10^{-13}$	296 ± 2	Sulbaek Anderson et al., 2004	RR (c,e)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO (or C_2H_5ONO)-NO-CF_3CHO-CH_3COCH_3-air mixtures at 1 bar pressure. The concentrations of CF_3CHO and CH_3COCH_3 were measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CF_3CHO)/k(HO + CH_3C(O)CH_3) = (2.43 \pm 0.53)$ is placed on an absolute basis by use of a rate coefficient of $k(HO + CH_3C(O)CH_3) = 1.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of O_2 in the presence of H_2 at 1 bar pressure. FTIR was used to monitor the disappearance of reactant and reference compound. The measured rate coefficient ratio of $k(HO + CF_3CHO)/k(HO + C_2H_6) = (2.00 \pm 0.13)$ is placed on an absolute basis by use of a rate coefficient of $k(HO + C_2H_6) = 2.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) HO radicals were generated by the photolysis of CH_3ONO in the presence of NO in air at a pressure of 933 mbar. The concentrations of CF_3CHO, C_2H_2, C_2H_4 and reaction products were measured by FTIR spectroscopy. The measured rate coefficient ratios $k(HO + CF_3CHO)/k(HO + C_2H_2)$ and $k(HO + CF_3CHO)/k(HO + C_2H_4)$ were placed on an absolute basis by using $k(HO + C_2H_2) = 8.45 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 296 K (Sørensen et al. 2003), and $k(HO + C_2H_4) = 8.52 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 296 K (Calvert et al. 2000).

(d) Relative to C_2H_2.

(e) Relative to C_2H_4.

Preferred Values

$k = 5.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute and relative rate coefficients of Sulbaek Andersen et al., 2004, Sellevåg et al. (2004) and Scollard et al. (1993). The rate coefficient data of Dóbé et al. (1989) was not used due to its large uncertainty.

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IV.A1.31

$HO + CF_3C(O)OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.6 \pm 0.4) \times 10^{-13}$	315	Møgelberg et al., 1994	PR-RA
$(1.5 \pm 0.2) \times 10^{-13}$	348		
Relative Rate Coefficients			
$3.73 \times 10^{-19}\ T^2 \exp[(375 \pm 400)/T]$	283-323	Carr et al. 1994	RR (a,b)
$(1.14 \pm 0.10) \times 10^{-13}$	298 ± 2		
$(1.21 \pm 0.22) \times 10^{-13}$	298 ± 2	Carr et al., 1994	RR (a,c)
$(1.75 \pm 0.44) \times 10^{-13}$	296	Møgelberg et al., 1994	RR (d)
$(8.70 \pm 1.44) \times 10^{-14}$	296 ± 2	Hurley et al., 2004	RR (e,f)
$(1.00 \pm 0.11) \times 10^{-13}$	296 ± 2	Hurley et al., 2004	RR (e,g)

Comments

(a) Relative rate method. HO radicals were generated by the 254 nm photolysis of O_3 in the presence of water vapor in O_3-H_2O-$CF_3C(O)OH$-C_2H_6 (or C_3H_8)-O_2 mixtures. The concentrations of $CF_3C(O)OH$ and C_2H_6 (or C_3H_8) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(HO + CF_3C(O)OH)/k(HO + C_2H_6) = 0.025 \exp[(874 \pm 400)/T]$ (0.47 ± 0.04 at 298 ± 2 K) and $k(HO + CF_3C(O)OH)/k(HO + C_3H_8) = 0.11 \pm 0.02$ at 298 K, are placed on an absolute basis by using rate coefficients of $k(HO + C_2H_6) = 1.5 \times 10^{-17}\ T^2 \exp(-499/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation) and $k(HO + C_3H_8) = 1.10 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(b) Relative to k(OH + ethane).

(c) Relative to k(OH + propane).

(d) Relative rate method. HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of H_2 in O_3-H_2-$CF_3C(O)OH$-C_2H_6-O_2 mixtures at 740 Torr total pressure. The concentrations of $CF_3C(O)OH$ and ethane were measured by FTIR spectroscopy. The measured rate coefficient ratio was $k(HO + CF_3C(O)OH)/k(HO + C_2H_6) = 0.59 \pm 0.04$. If the $(CF_3C(O)OH)_2$ dimer is unreactive towards the HO radical, then the rate coefficient ratio corrected for dimer formation is 0.84 ± 0.06. An average value of $k(HO + CF_3C(O)OH)/k(HO + C_2H_6) = 0.72 \pm 0.18$ was preferred and is placed on an absolute basis by using a rate coefficient of $k(HO + C_2H_6) = 2.43 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

(e) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO in the presence of NO in air. CH_3ONO-NO-$CF_3C(O)OH$-reference compound-air mixtures at 700 Torr total pressure were photolysed by UV lamps. Reference compounds were C_2H_2 and C_2H_4. The concentrations of $CF_3C(O)OH$, C_2H_2 and C_2H_4 were measured by FTIR spectroscopy. The measure rate constant ratios of $k(HO + CF_3C(O)OH)/k(HO + C_2H_2) = 0.103 \pm 0.017$ and $k(HO + CF_3C(O)OH)/k(HO + C_2H_4) = 0.0116 \pm 0.0012$ are placed on an absolute basis by using rate coefficients of $k(HO + C_2H_2) = 8.45 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Sørensen et al., 2003) and $k(HO + C_2H_4) = 8.66 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Calvert et al. 2000), both at 296 K and 700 Torr of air.

(f) Relative to k(HO + acetylene).

(g) Relative to k(HO + ethene).

Preferred Values

$k = 1.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 280-350 K.

Reliability

$\Delta \log k = \pm 0.1$ over the temperature range 280-350 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the relative and absolute rate coefficients of Møgelberg et al. (1994), Carr et al. (1994) and Hurley et al. (2004). The reaction is expected to proceed by overall H-atom abstraction from the -OH group to form $H_2O + CF_3CO_2$ (see the data sheets on the HO radical reactions with HC(O)OH and $CH_3C(O)OH$).

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IV.A1.32

$$\mathbf{HO_2 + CH_2FO_2 \rightarrow O_2 + CH_2FO_2H \quad (1)}$$
$$\mathbf{\rightarrow O_2 + HCOF + H_2O \quad (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Branching Ratios			
$k_1/k = 0.29 \pm 0.08$	295	Wallington et al., 1994	UVP-FTIR (a)
$k_2/k = 0.71 \pm 0.11$	295		

Comments

(a) HO_2 and CH_2FO_2 radicals were generated from the steady-state photolysis of Cl_2 in the presence of CH_3F-H_2-air mixtures at total pressures of 400–933 mbar. The branching ratios were derived from FTIR analysis of CH_2FO_2H and HCOF, which accounted for 100 ± 13% of the loss of CH_3F.

Preferred Values

$k_1/k = 0.3$ at 298 K.
$k_2/k = 0.7$ at 298 K.

Reliability

$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The lack of a pressure dependence of the branching ratio determined by Wallington et al. (1994) indicates that there is no thermal decomposition of the products. The observation of two reaction channels for this reaction is in accord with data for other HO_2 reactions with substituted peroxy radicals, for example, with $HOCH_2O_2$ and $CH_3OCH_2O_2$ radicals.

References

Wallington, T. J., Hurley, M. D., Schneider, W. F., Sehested, J. and Nielsen, O. J.: Chem. Phys. Lett. 218, 34, 1994.

IV.A1.33

$$\mathbf{HO_2 + CF_3O_2 \rightarrow CF_3O_2H + O_2 \quad (1)}$$
$$\mathbf{\rightarrow C(O)F_2 + HOF + O_2 \quad (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Branching Ratios			
$\leq 2 \times 10^{-12}$	296	Hayman and Battin-Leclerc, 1995	FP-UVA (a)
$(4.0 \pm 2.0) \times 10^{-12}$	295	Sehested et al., 1997	PR-UVA (b)
$\leq 3 \times 10^{-12}$	296	Biggs et al., 1997	DF-LIF (c)

Comments

(a) Flash photolysis of H_2O_2 in the presence of CF_3CH_2F-O_2-N_2 mixtures at a total pressure of 1013 mbar. Primary investigation of CF_3CHFO_2 radical kinetics, with CF_3O_2 radicals generated from the decomposition of product CF_3CHFO radicals. Decays in transient absorption signals (with contributions from CF_3CHFO_2, HO_2 and CF_3O_2) were recorded in the wavelength range 220 nm to 240 nm. Upper limit k derived from simulations of the decay traces using a 15 reaction mechanism. Good fits could not be obtained if the CF_3O_2 + HO_2 was occurring appreciably under the experimental conditions.

(b) Pulse radiolysis study of CHF_3-H_2-O_2-SF_6 mixtures at a total pressure of 1013 mbar. CF_3O_2 and HO_2 radicals were monitored by UV absorption spectroscopy at 230 nm. Decays in transient absorption signals (with contributions from HO_2 and CF_3O_2) were recorded at 230 nm. The cited value of k was derived from simulation of the decay in absorption, using a 13 reaction chemical mechanism.

(c) Experiments performed at 2.7 mbar. CF_3O_2 and HO_2 radicals were produced by the F + CHF_3 and F + CH_3OH reactions, with subsequent addition of O_2. Both CF_3O_2 and HO_2 were monitored by titration to NO_2 following reaction with excess NO, with detection of NO_2 by LIF. Upper limit k derived from simulations of the decay in radical concentration, using an explicit reaction mechanism. Actual values obtained varied in the range $< (1\text{–}3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

No recommendation

Comments

Although the results of Sehested et al. (1997) and Biggs et al. (1997) provide evidence for the occurrence of the reaction of HO_2 with CF_3O_2, the rate coefficient is not well-determined in any of the reported studies. No recommendation can be made until further kinetics and product studies of this reaction are available.

References

Biggs, P., Canosa-Mas, C.E., Shallcross, D.E., Vipond, A. and Wayne, R.P.: J. Chem. Soc. Farad. Trans. 93, 2701, 1997.
Hayman, G. and Battin-Leclerc, F.: J. Chem. Soc. Farad. Trans. 91, 1313, 1995.
Sehested, J., Møgelberg, T., Fagerstrom, K., Mahmoud, G. and Wallington, T. J.: Int. J. Chem. Kinet. 29, 673, 1997.

IV.A1.34

$$\begin{aligned} \mathbf{HO_2 + CF_3CHFO_2} &\rightarrow \mathbf{O_2 + CF_3CHFO_2H} \quad &\mathbf{(1)} \\ &\rightarrow \mathbf{O_2 + CF_3C(O)F + H_2O} \quad &\mathbf{(2)} \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.8 \times 10^{-13} \exp[(910 \pm 220)/T]$	210-363	Maricq et al., 1994	FP-UVA (a)
$(4.7 \pm 1.7) \times 10^{-12}$	295		
$(4.0 \pm 2.0) \times 10^{-12}$	296	Hayman and Battin-Leclerc, 1995	LP-UVA (b)
$(3.3 \pm 1.5) \times 10^{-12}$	323		
$(2.4 \pm 1.5) \times 10^{-12}$	373		
$(5.0 \pm 1.5) \times 10^{-12}$	295	Sehested et al., 1997	PR-UVA (c)
Branching Ratios			
$k_1/k > 0.95$	296	Maricq et al., 1994	UVP-FTIR (d)
$k_2/k < 0.05$	296		

Comments

(a) Flash photolysis time-resolved UV absorption study of F_2-CF_3CH_2F-H_2-O_2-N_2 mixtures. The rate coefficients were obtained from a fit of the decay curves for CF_3CHFO_2, HO_2, CF_3O_2 and ROOH, based on a mechanism of 14 reactions.

(b) Flash photolysis of H_2O_2 in the presence of CF_3CH_2F-O_2-N_2 mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from CF_3CHFO_2, HO_2 and CF_3O_2) were recorded in the wavelength range 220 nm to 240 nm. k derived from simulations of the decay traces using a 15 reaction mechanism.

(c) Pulse radiolysis study of CF_3CH_2F-H_2-O_2-SF_6 mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from CF_3CHFO_2, HO_2 and CF_3O_2) were recorded at 230 nm and 240 nm. The cited value of k was derived from simulation of the decay in absorption, using a 22 reaction chemical mechanism.

(d) Steady-state photolysis of Cl_2-CF_3CH_2F-H_2-O_2-N_2 mixtures with FTIR analysis of the products HC(O)F, $CF_3C(O)F$, $C(O)F_2$ and $CF_3O_3CF_3$. The branching ratio, k_2/k, cited above was based on measurements of CF_3COF, and the value of k_1/k was inferred.

Preferred Values

$k = 4.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.0 \times 10^{-13} \exp(910/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210-365 K.
$k_1/k = 1.0$ at 298.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 300$ K.
$\Delta (k_1/k) = ^{+0.0}_{-0.1}$ at 298 K.

Comments on Preferred Values

The preferred value of k at 298 K is the average of the results of Maricq et al. (1994) (based on their Arrhenius expression), Hayman and Battin-Leclerc (1995) and Sehested et al. (1997). The results of these studies are in good agreement, even though k

was necessarily extracted from simulations of complex systems. The preferred Arrhenius expression for k is based on the E/R value from the study of Maricq et al. (1994), combined with a pre-exponential factor adjusted to give the preferred value of k at 298 K. The results of Hayman and Battin-Leclerc (1995) at 323 K and 373 K are also consistent with this recommendation. The preferred branching ratios are based on those reported by Maricq et al. (1994), which require confirmation.

It is interesting to note that k is approximately a factor of two smaller than that recommended for the reaction of HO_2 with $C_2H_5O_2$. This confirms a deactivating influence of α-F and α-CF_3 groups, observed for the reactions of a number of halogenated peroxy radicals with HO_2.

References

Hayman, G. and Battin-Leclerc, F.: J. Chem. Soc. Faraday Trans. 91, 1313, 1995.
Maricq, M. M., Szente, J. J., Hurley, M. D. and Wallington, T. J.: J. Phys. Chem. 98, 8962, 1994.
Sehested, J., Møgelberg, T., Fagerstrom, K., Mahmoud, G. and Wallington, T. J.: Int. J. Chem. Kinet. 29, 673, 1997.

IV.A1.35

$$\begin{aligned} \mathbf{HO_2 + CF_3CF_2O_2} &\rightarrow \mathbf{O_2 + CF_3CF_2O_2H} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{O_2 + CF_3C(O)F + HOF} \quad \mathbf{(2)} \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.6) \times 10^{-12}$	296	Hayman and Battin-Leclerc, 1995	LP-UVA (a)

Comments

(a) Flash photolysis of H_2O_2 in the presence of CF_3CHF_2-O_2-N_2 mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from $CF_3CF_2O_2$, HO_2 and CF_3O_2) were recorded in the wavelength range 220 nm and 230 nm. k derived from simulations of the decay traces using a 16 reaction mechanism.

Preferred Values

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

Reliability

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

Comments on Preferred Values

While the above value of the rate coefficient seems reasonable, it has been derived from the analysis of a complex chemical system and requires independent verification to reduce the recommended error limits. It is interesting to note that k is substantially smaller than that recommended for the reaction of HO_2 with $C_2H_5O_2$. This confirms a deactivating influence of α-F and α-CF_3 groups, observed for the reactions of a number of halogenated peroxy radicals with HO_2.

References

Hayman, G. and Battin-Leclerc, F.: J. Chem. Soc. Faraday Trans. 91, 1313, 1995.

IV.A1.36

$FO_2 + CO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$< 5.1 \times 10^{-16}$	298	Sehested et al., 1994	PR-UVA (a)

Comments

(a) Pulse radiolysis of CO-O_2-SF_6 mixtures in a high pressure cell at 18 bar SF_6. The decay of FO_2 radicals was monitored in absorption at 220 nm.

Preferred Values

$k < 6 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred room temperature upper limit is based on results of the pulse radiolysis-UV absorption study of Sehested et al. (1994). This is the sole reported study of this reaction.

References

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

IV.A1.37

$FO_2 + CH_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$< 4 \times 10^{-15}$	298	Sehested et al., 1994	(a)

Comments

(a) Pulse radiolysis/UV absorption spectroscopy technique. Pulse radiolysis of CH_4-O_2-SF_6 mixtures in a high pressure cell at 18 bar SF_6. The decay of FO_2 radicals was monitored in absorption at 220 nm.

Preferred Values

$k < 4.1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred room temperature upper limit is based on results of the pulse radiolysis-UV absorption study of Sehested et al. (1994). This is the sole reported study of this reaction rate coefficient.

References

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

IV.A1.38

$$\mathbf{CF_3 + O_2 + M \rightarrow CF_3O_2 + M}$$

$\Delta H^\circ(1)$ = -148 kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.1) \times 10^{-29}$ [He]	295	Ryan and Plumb, 1982	DF-MS (a)
$(1.9 \pm 0.2) \times 10^{-29}$ $(T/300)^{-4.7}$ [N$_2$]	233-373	Caralp et al., 1986	PLP-MS (b)
$(2.5 \pm 0.3) \times 10^{-29}$ [N$_2$]	295	Breheny et al., 2001	PLP-CL (c)

Comments

(a) Microwave discharge-flow system coupled to quadrupole MS. CF$_3$ radicals monitored by MS. Measurements over the range 0.7–11 mbar, extrapolated with $F_c \approx 0.4$ and $k_\infty \approx 8.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(b) Pulsed laser photolysis-MS study over the range 0.3–16 mbar. Extrapolation with $F_c \approx 0.6$ and $k_\infty \approx 9.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(c) Pulsed laser photolysis-IR chemiluminescence study of CF$_3$I in the presence of NO$_2$ and O$_2$, using IR emission from the reaction CF$_3$ + NO$_2$ for detection. Pressure range 2.7–150 mbar. Extrapolation with $F_c \approx 0.6$ and $k_\infty \approx 2.55 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, using data up to 800 mbar from relative rate measurements by Kaiser et al. (1995).

Preferred Values

$k_0 = 2.2 \times 10^{-29}$ $(T/300)^{-4.7}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 230–380 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 an average of the low pressure results from Caralp et al. (1986), and Breheny et al. (2001) which appear well consistent with the measurements in He from Ryan and Plumb (1982). Differences in k_∞ and F_c, used in the extrapolation, only slightly influence the preferred k_0 because all measurements extended to pressures close to the low pressure limit of k.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.0×10^{-11}	298	Cooper et al., 1980	PR (a)
Relative Rate Coefficients			
$(3.92 \pm 0.25) \times 10^{-12}$	271-363	Kaiser et al., 1995	PR (b)

Comments

(a) Pulse radiolysis of CF_3Cl. CF_3O_2 detected by UV absorption spectroscopy near 260 nm. Measurements in 920 mbar of Ar.

(b) UV irradiation of CF_3I-CH_4-Cl_2-N_2-O_2 mixtures and observation of loss of CF_3 and CH_4. Measurement of the ratio $k(CF_3 + O_2)/k(CF_3 + Cl_2)$ as a function of the pressure and calibration of this ratio at low pressures against $k_0(CF_3 + O_2)$ from Caralp et al. (1986). Inspection of the spectra recorded by Cooper et al. (1980) and comparison with more recently detected spectra of CF_3O_2 indicates that the rate of $CF_3 + O_2$ was not observed by Cooper et al. (1980).

Preferred Values

$k_\infty = 4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 1.5$.

Comments on Preferred Values

Since the measurements of Cooper et al. (1980) were shown not to lead to k_∞, the results from the relative rate measurements from Kaiser et al. (1995) are preferred. They are similar as values for k_∞ for $CCl_3 + O_2$ from Luther et al. (2001) for which $n = -1.4$ was measured. Using an estimated $F_c = 0.39$ independent of the temperature, all results (except those from Cooper et al. (1980)) are consistently represented and the remaining uncertainty of k_∞ does not impact on k_0.

References

Breheny, C., Hancock, G. and Morrell, C.: Z. Phys. Chem., 215, 305, 2001.
Caralp, F., Lesclaux, R. and Dognon, A. M.: Chem. Phys. Lett., 129, 433, 1986.
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Kaiser, E. W., Wallington, T. J. and Hurley, M. D.: Int. J. Chem. Kinet., 27, 205, 1995.
Luther, K., Oum, K. and Troe, J.: J. Phys. Chem. A, 105, 5535, 2001.
Ryan, K. R. and Plumb, I. C.: J. Phys. Chem., 86, 4678, 1982.

IV.A1.39

$$\mathbf{CF_3O + O_2 \rightarrow COF_2 + FO_2}$$

$\Delta H°(1) = 47.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<2 \times 10^{-17}$	298	Turnipseed et al., 1994	PLP/LIF (a)
$<4 \times 10^{-17}$	373		

Comments

(a) CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.

Preferred Values

$k < 1 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k < 1 \times 10^{-10}$ exp(-5600/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250-370 K.

Comments on Preferred Values

The preferred values are based on the upper limit at 373 K reported by Turnipseed et al. (1994). Assuming that the activation energy barrier is at least equal to the reaction endothermicity (5600 K) leads to the preferred limits given for the A-factor and for k(298 K). This procedure using the high temperature limit yields a room temperature limit an order of magnitude lower than the upper limit to the rate coefficient directly determined at 298 K. Chen et al. (1992) in a long path FTIR study of the reaction of CF_3O with NO found no evidence for the reaction of CF_3O with O_2 in 1 bar of air at room temperature.

References

Chen, J., Zhu, T. and Niki, H.: J. Phys. Chem., 96, 6115, 1992.
Turnipseed, A. A., Barone, S. B. and Ravishankara, A. R.: J. Phys. Chem., 98, 4594, 1994.

IV.A1.40

$$\mathbf{CF_3O + O_3 \rightarrow CF_3O_2 + O_2}$$

$\Delta H^\circ(1) = -101.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<1 \times 10^{-13}$	295	Nielsen and Sehested, 1993	PR/UVA (a)
$<5 \times 10^{-14}$	210-353	Maricq and Szente, 1993	FP/UVA (b)
$<2 \times 10^{-15}$	298	Fockenberg et al., 1994	LP/LIF (c)
$<4 \times 10^{-14}$	298	Ravishankara et al., 1994	FT/CIMS (d)
$(2.5 \pm 0.7) \times 10^{-14}$	298	Turnipseed et al., 1994	PLP/LIF (e)
$(3.7 \pm 1.5) \times 10^{-14}$	373		
$(2.8 \pm 0.5) \times 10^{-15}$	298	Meller and Moortgat, 1995	(f)
$(1.3 \pm 0.5) \times 10^{-14}$	298	Bourbon et al., 1996	FT/LIF (g)
Relative Rate Coefficients			
$<3 \times 10^{-14}$	295	Wallington et al., 1993	RR (h)
$(1.5 \pm 0.5) \times 10^{-14}$	296	Wallington and Ball, 1995	(i)

Comments

(a) Radicals generated by pulse radiolysis of CHF_3-O_2-O_3-SF_6 mixtures. Upper limit for k derived from simulations of ozone absorption transients at 254 nm and 276 nm in the presence of CF_3O and CF_3O_2 radicals.

(b) Radicals generated by 351 nm photolysis of F_2 in a flowing F_2-CHF_3-O_3-O_2-N_2 mixture. O_3 and CF_3O_2 radicals were monitored by absorption at 255 nm and 210 nm respectively.

(c) CF_3O radicals were generated by excimer laser photolysis of CF_3OCl at 351 nm.

(d) CF_3O radicals were generated by pyrolysis of CF_3OOCF_3.

(e) CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.

(f) Static photolysis of CF_3OOCF_3 in the presence of O_3; Analysis of CF_3O and $CF_3OO_3CF_3$ products by FTIR. k determined by analysis of complex mechanism.

(g) CF_3O radicals were generated by pyrolysis of CF_3OOCF_3.

(h) Radicals generated by visible photolysis of CF_3NO/O_3 mixtures in 700 torr O_2. Analysis was by FTIR spectrometer. Value of k was derived by authors from the measured ratio $k/k(CF_3O + NO_2)$ and an estimated value of $k(CF_3O + NO_2)$.

(i) Relative rate technique using FTIR. k measured relative to $k(CF_3O + CH_4) = 2.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

Preferred Values

$k = 1.8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2 \times 10^{-12} \exp(-1400/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.

Reliability

$\Delta \log k = \pm 1$ at 298 K.
$\Delta (E/R) = \pm 600$ K.

Comments on Preferred Values

The preferred value of k at 298 K is an average of the room temperature results of Turnipseed et al. (1994), Wallington and Ball (1995) and Bourbon et al (1996). Fockenberg et al. (1994) and Meller and Moortgat (1995) reported room temperature values an order of magnitude lower. The reason for this discrepancy is unknown, although both studies appear to have possibilities for interference by secondary chemistry. Upper limits reported in the studies of Nielsen and Sehested (1993), Maricq and Szente (1993), Ravishankara et al. (1994) and Wallington et al. (1993) are all consistent with the recommendation. Because of the large uncertainties in the two values of Turnipseed et al. (1994), Arrhenius parameters have not been derived using these values. Rather, the recommended A factor has been estimated by analogy with other CF_3O reactions, and the value of E/R fitted to the preferred room temperature value.

References

Bourbon, C., Brioulov, M. and Devolder, P.: C. A. Acad. Sci..Paris, 322, 181, 1996.
Fockenberg, C., Saathoff, H. and Zellner, R.: Chem. Phys. Lett., 218, 21, 1994.
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Nielsen, O. J. and Sehested, J.: Chem. Phys. Lett., 213, 433, 1993.
Ravishankara, A. R., Turnipseed, A. A., Jensen, N. R., Barone, S., Mills, M., Howard, C. J. and Solomon, S.: Science, 263, 71, 1994.
Turnipseed, A. A., Barone, S. B. and Ravishankara, A. R.: J. Phys. Chem., 98, 4594, 1994.
Wallington, T. J. and Ball, J. C.: Chem. Phys. Lett., 234, 187, 1995.
Wallington, T. J., Hurley, M. D. and Schneider, W. F.: Chem. Phys. Lett., 213, 442, 1993.

IV.A1.41

$$CF_3O + H_2O \rightarrow CF_3OH + HO$$

$\Delta H°(1) = 43.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<1 \times 10^{-16}$	298	Turnipseed et al., 1995	(a)
$<2 \times 10^{-16}$	381		
Relative Rate Coefficients			
$>2 \times 10^{-18}$	296	Wallington et al., 1993	(b)
$<4 \times 10^{-16}$	296		

Comments

(a) Pulsed laser photolysis/pulsed laser induced fluorescence technique. CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.

(b) Long path FTIR-based study. CF_3O radicals generated by chlorine-initiated oxidation of CF_3CFH_2 (HFC-134a) in photolytic mixture of Cl_2-CF_3CFH_2-H_2O in 1 bar air. Reaction rate studied in competition with the rate of $CF_3O + CF_3CFH_2$.

Preferred Values

$k < 2 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k < 3 \times 10^{-12} \exp(-3600/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-380 K.

Comments on Preferred Values

The A-factor is estimated by analogy with similar reactions of CF_3O and the activation energy is fitted to the upper limit at 381 K reported by Turnipseed et al. (1995). Note that this procedure results in a lower limit for E/R ($E/R > 3600$ K). The preferred value of k(298 K) is calculated from the Arrhenius parameters. The limits reported by Wallington et al. (1993) are consistent with this preferred value.

References

Turnipseed, A. A., Barone, S. B., Jensen, N. R., Hanson, D. R., Howard, C. J. and Ravishankara, A. R.: J. Phys. Chem., 99, 6000 , 1995.
Wallington, T. J., Hurley, M. D., Schneider, W. F., Sehested, J. and Nielsen, O. J.: J Phys. Chem., 97, 7606, 1993.

IV.A1.42

$CF_3O + NO \rightarrow COF_2 + FNO$

ΔH° = -135 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.2 \pm 2.7) \times 10^{-11}$	295	Sehested and Nielsen, 1993	PR/UVA (a)
$3.34 \times 10^{-11} \exp[(160 \pm 45)/T]$	233-360	Turnipseed et al., 1994	PLP/LIF (b)
$(5.62 \pm 0.74) \times 10^{-11}$	298		
$4.1 \times 10^{-11} \exp[(60 \pm 100)/T]$	231-393	Jensen et al., 1994	(c)
$(5.0 \pm 1.0) \times 10^{-11}$	298		
$(4.7 \pm 0.9) \times 10^{-11}$	298	Bourbon et al., 1996	DF/LIF (d)
$(4.72 \pm 0.30) \times 10^{-11}$	293	Bhatnagar and Carr, 1994	FP/MS (e)
$4.1 \times 10^{-11} \exp[(60 \pm 100)/T]$	213-253	Dibble et al., 1995	LP/TDLS (f)

Comments

(a) Radicals generated by pulse radiolysis of CHF_3-O_2-NO-SF_6 mixtures. Value of k derived from simulations of FNO absorption transients at 310.5 nm.

(b) CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.

(c) Flow tube reactor/chemical ionization mass spectrometer technique. CF_3O radicals were generated by pyrolysis of CF_3OOCF_3. A low value of k from the same laboratory reported earlier by Bevilacqua et al. (1993) is superseded by these results.

(d) CF_3O radicals were generated by DF technique in F/CF_3H/O_2/NO system.

(e) k obtained by modeling NO time dependence during secondary reactions in CF_3O_2 + NO reaction.

(f) CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm. Time resolved formation of COF_2 using tunable diode laser absorption near 1950 cm^{-1}. FNO identified as major co-product with COF_2.

Preferred Values

$k = 5.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.7 \times 10^{-11} \exp(110/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-390 K.

Reliability

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

Comments on Preferred Values

The preferred values are based on the 233–360 K values of Turnipseed et al. (1994), the 231–393 K values of Jensen et al. (1994) and the 295 K value of Sehested and Nielsen (1993). These results are in good agreement. The low value of k reported by Bevilacqua et al. (1993) has been superseded by the results of Jensen et al. (1994). Room temperature results from Bourbon et al. (1996) and Bhatnagar and Carr (1994) and a temperature dependence study of Dibble et al (1995) are in good agreement with the recommendation. The reaction products have been reported by Chen et al. (1992), Bevilacqua et al. (1993) and Li and Francisco (1991).

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IV.A1.43

$CF_3O + CH_4 \rightarrow CF_3OH + CH_3$

$\Delta H°(1) = -16.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.2) \times 10^{-14}$	298	Saathoff and Zellner, 1993	LP/LIF (a)
$1.92 \times 10^{-12} \exp[-(1370 \pm 85)/T]$	247-360	Barone et al., 1994	PLP/LIF (b)
$(1.93 \pm 0.11) \times 10^{-14}$	298		
$3.1 \times 10^{-12} \exp[-(1470 \pm 250)/T]$	231-385	Jensen et al., 1994	DF/CIMS (c)
$(2.2 \pm 0.4) \times 10^{-14}$	298		
$4.49 \times 10^{-12} \exp[-(1606 \pm 84)/T]$	296-573	Bourbon et al., 1995	DF/LIF (d)
$(2.05 \pm 0.20) \times 10^{-12}$	298		
$3.3 \times 10^{-12} \exp[-(1430 \pm 150)/T]$	235-401	Bednarek et al., 1995	LP/LIF (e)
2.5×10^{-14}	298		
Relative Rate Coefficients			
$<5 \times 10^{-15}$	297	Chen et al., 1992	(f)
$(1.2 \pm 0.1) \times 10^{-14}$	298	Kelly et al., 1993	(g)

Comments

(a) CF_3O radicals were generated by photolysis of CF_3OF at 248 nm.

(b) CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.

(c) CF_3O radicals were generated by pyrolysis of CF_3OOCF_3.

(d) CF_3O radicals were generated by the pyrolysis of CF_3OOCF_3.

(e) CF_3O radicals were generated by photolysis of CF_3OF at 248 nm.

(f) Long path FTIR-based product study of visible photolysis of CF_3NO-NO-CH_4 mixtures in 700 torr air. Searched for CH_2O product from oxidation of CH_4 initiated by reaction of CF_3O radicals with CH_4. Upper limit of k given in table is derived from the measured ratio $k/k(CF_3O+NO) < 10^{-4}$ and the value of $k(CF_3O+NO)$ given in this evaluation.

(g) Long-path FTIR-based study. CF_3O radicals were generated by photolysis of CF_3OOCF_3. The decay of the reactant hydrocarbon was compared with the decay of the reference hydrocarbon. The value of k given in table is derived from the measured ratio $k/k(CF_3O + C_2H_6) = 0.010 \pm 0.001$ and the value of $k(CF_3O+C_2H_6)$ (IUPAC, current evaluation).

Preferred Values

$k = 2.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.6 \times 10^{-12} \exp(-1420/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-380 K.

Reliability

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

Comments on Preferred Values

The preferred value at room temperature is the average of the values reported by Saathoff and Zellner (1993), Barone et al. (1994), Jensen et al. (1994), Bourbon et al. (1995) and Bednarek et al. (1994). Results of these direct studies are in excellent agreement at room temperature. The temperature dependence is based on the 247–360 K data of Barone et al. (1994), the 231–385 K data of Jensen et al. (1994) and the 235–401 K data of Bednarek et al. (1994). The temperature dependence of Bourbon et al. (1995) is thought to be high due to possible influence of wall reaction at high temperature. The relative rate measurements of Chen et al. (1992) and Kelly et al. (1993) are factors of 4 and 2, respectively, lower than the preferred value. Wallington and Ball (1995) reported $k/k(CF_3O + C_2H_6) = 0.0152 \pm 0.0023$ at 296 K in good agreement with the recommended rate coefficients. Jensen et al. (1994) detected the product CF_3OH by chemical ionization mass spectrometer (CIMS) and observed its formation to correlate with the loss of the CF_3O reactant. The CF_3OH product of this reaction was also observed by Bevilacqua et al. (1993) and also by Bednareck et al. (1994), who used FTIR spectroscopy to show that CF_3OH is converted slowly to $C(O)F_2$.

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IV.A1.44

$CF_3O + C_2H_6 \rightarrow CF_3OH + C_2H_5$

$\Delta H°(1) = -32.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.2) \times 10^{-12}$	298	Saathoff and Zellner, 1993	(a)
4.84×10^{-12} exp[-(400 ± 70)/T]	233-360	Barone et al., 1994	(b)
$(1.30 \pm 0.11) \times 10^{-12}$	298		
1.13×10^{-11} exp[-(642 ± 113)/T]	295-573	Bourbon et al., 1995	(c)
$(1.31 \pm 0.13) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(1.1 \pm 0.6) \times 10^{-12}$	297	Chen et al., 1992	(d)

Comments

(a) Laser photolysis/laser induced fluorescence technique. CF_3O radicals were generated by the photolysis of CF_3OF at 248 nm.

(b) Pulsed laser photolysis/pulsed laser induced fluorescence technique. CF_3O radicals were generated by the photolysis of CF_3OOCF_3 at 193 nm.

(c) Fast flow tube (~1.3 mb pressure)/laser induced fluorescence. CF_3O radicals were generated by the pyrolysis of CF_3OOCF_3 at 193 nm.

(d) Long path FTIR-based product study of visible photolysis of CF_3NO-NO-C_2H_6 mixtures in 700 Torr air. The upper limit of k given in table is derived from measured ratio $k/k(CF_3O+NO) = 0.02 \pm 0.006$ and the value of $k(CF_3O+NO)$ (IUPAC, current recommendation).

Preferred Values

$k = 1.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.9 \times 10^{-12}$ exp($-400/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 230-360 K.

Reliability

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

Comments on Preferred Values

The preferred value at room temperature is the average of the values reported by Saathoff and Zellner (1993), Barone et al. (1994) and Bourbon et al. (1995). Results of these direct studies are in excellent agreement. The temperature dependence is based on the 233–360 K data of Barone et al. (1994). The temperature dependence of Bourbon et al. (1995) is thought to be high due to possible influence of wall reaction at high temperature. The relative rate measurement of Chen et al. (1992) is in good agreement with the preferred value. Kelly et al. (1993) used a relative rate method with FTIR detection to determine the rate of CF_3O reaction with a number of hydrocarbons relative to the rate of the reaction of CF_3O with C_2H_6. They reported $k(CF_3O + CH_4)/k = 0.010 \pm 0.001$ at 298 K and 1 bar pressure (Kelly et al., 1993). This is nearly a factor of 2 lower than the ratio of the preferred values given in this evaluation (0.017). Wallington and Ball (1995) reported $k(\mathrm{CF_3O + CH_4})/k = 0.0152 \pm 0.0023$ at 296 K in good agreement with the recommended rate coefficients.

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IV.A1.45-54

$$R_1(R_2)CHO + O_2 \rightarrow R_1COR_2 + HO_2 \text{ (or} \rightarrow \text{products)} \quad (1)$$

$$R_1(R_2)CHO\ (+ M) \rightarrow \text{products} \quad (2)$$

R = alkyl, halogenated alkyl, H or halogen atom

Rate coefficient data

Reaction Number	Reactions		k_1/k_2 cm^3 molecule^{-1}	Temp./K	Reference	Comments
IV.A1.45	$CH_2FO + O_2 \rightarrow HCOF + HO_2$	(1)	$k_1[O_2] \gg k_2$ (933 mbar, air)	298	Edney and Driscoll, 1992	(a)
IV.A1.46	$CH_2FO + M \rightarrow HCOF + H + M$	(2)	$k_1[O_2] \gg k_2$ (986 mbar, air)	298	Tuazon and Atkinson, 1993a	(a)
IV.A1.47	$CH_3CF_2O + O_2 \rightarrow$ products	(1)	$k_1[O_2] \ll k_2$ (933 mbar, air)	298	Edney and Driscoll, 1992	(b)
IV.A1.48	$CH_3CF_2O + M \rightarrow CH_3 + COF_2 + M$	(2)	$k_1[O_2] \ll k_2$ (986 mbar, air)	298	Tuazon and Atkinson, 1993a	(c)
IV.A1.49	$CH_2FCHFO + O_2 \rightarrow CH_2FCOF + HO_2$	(1)	$k_1[O_2] \ll k_2$ (933 mbar, air)	296	Wallington et al., 1994	(d)
IV.A1.50	$CH_2FCHFO + M \rightarrow CH_2F + HCOF + M$	(2)				
IV.A1.51	$CF_3CHFO + O_2 \rightarrow CF_3COF + HO_2$	(1)	$1.58 \times 10^{-25} \exp(3600/T)$	296	Wallington et al., 1992	(e)
IV.A1.52	$CF_3CHFO + M \rightarrow CF_3 + HCOF$	(2)	2.8×10^{-20} (2 bar)	298		
			$3.2 \times 10^{-25} \exp(3510/T)$	273-320	Tuazon and Atkinson, 1993b	(f)
			4.5×10^{-20} (986 mbar)	298		
			$k_2 = 3.7 \times 10^7 \exp(-2200/T) s^{-1}$	211-372	Maricq and Szente, 1992	(g)
			$k_2 = 2.3 \times 10^4\ s^{-1}$ (307 mbar)	298		
			$1.18 \times 10^{-24} \exp(2860/T)$	235-318	Rattigan et al., 1994	(h)
			1.7×10^{-20} (1 bar)	298		
			1.5×10^{-19} (50 mbar)	295	Bednarek et al, 1996	(i)
			$k_1 = 2.7 \times 10^{-15}$	295		
			$8.7 \times 10^{-25} \exp(3240/T)$ (1 bar)	244-295		
			$2.1 \times 10^{-25} \exp(3625/T)$ (1 bar)	238-295	Wallington et al, 1996	(j)
			$3.8 \times 10^{-24} \exp(2400/T)$ (1 bar)	298-357	Hasson et al, 1998	(k)
IV.A1.53	$CF_3CF_2O + O_2 \rightarrow$ products	(1)	$k_1[O_2] \ll k_2$ (933 mbar, air)	298	Edney and Driscoll, 1992	(l)
IV.A1.54	$CF_3CF_2O + M \rightarrow CF_3 + CF_2O + M$	(2)	$k_1[O_2] \ll k_2$ (986 mbar, air)	298	Tuazon and Atkinson, 1993a	(m)

Comments

(a) Steady-state photolysis of Cl_2 in the presence of CH_3F-air mixtures (1 atm) with FTIR absorption spectroscopic analysis: a 100% yield of HCOF was observed, consistent with $k_1[O_2] \gg k_2$.

(b) Steady-state photolysis of Cl_2 in the presence of CH_3CHF_2-air mixtures (1 atm) with FTIR absorption spectroscopic analysis: a 100 ± 5% yield of COF_2 was observed, consistent with $k_1[O_2] \ll k_2$.

(c) Similar experiments to those of Comment (b); a 92.2 ± 1.2 % yield of COF_2, plus other unidentified products, was observed, consistent with $k_1[O_2] \ll k_2$.

(d) Steady-state photolysis of Cl_2 in the presence of CH_2FCH_2F-air mixtures (933 mbar) with FTIR analysis: a 91± 10% yield of HCOF was observed, consistent with $k_1[O_2] \ll k_2$.

(e) Steady-state photolysis of Cl_2 in the presence of CF_3CFH_2-O_2-N_2 mixtures at total pressures of 2 atm with FTIR analysis of products CF_3COF and HCOF. The ratio k_1/k_2 was found to be pressure dependent over the range 27–732 mbar but approximately independent of pressure above 933 mbar.

(f) Similar experiments to those of Comment (e) at a total pressure of 986 mbar.

(g) Flash-photolysis time-resolved UV absorption spectroscopic study of CF_3CHFO_2 radicals from F_2-CF_3CH_2F-O_2-N_2 mixtures, k_1 obtained from a fit of CF_3O_2 formation profiles, produced from reaction (1) followed by $CF_3 + O_2 + M$. Experiments were carried out at a total pressure of 306 mbar, well below the high-pressure limit.

(h) Cl_2- initiated photooxidation of CF_3CH_2F at 1atm pressure, with dual-beam diode-array UV spectroscopic determination of CF_3COF and HCOF products.

(i) Direct time-resolved experiment using laser pulsed photolysis-laser long path absorption; CF_3CFHO produced by CF_3CFHO_2 + NO reaction and kinetics of thermal decomposition reaction determined at p = 50 mbar and 295 K. The relatve rate ratio cited for k_1/k_2 was determined in a second experiment carried out over the temperature range 244–295 K and p = 1 bar, using UV photolysis and FTIR analysis of products.

(j) Steady-state photolysis of Cl_2 in the presence of CF_3CFH_2-O_2-N_2 mixtures at total pressures of 55–800 mbar with FTIR analysis of products CF_3COF and HCOF. Experiments also carried out with NO present so that CF_3CFHO was produced by CF_3CFHO_2 + NO reaction, as opposed to the self reaction of CF_3CFHO_2. The ratio k_1/k_2 was found to increase with pressure over the range given but approximately independent of pressure above 1500 mbar. The ratio k_1/k_2 was significantly lower in the NO experiments. This was ascribed to the production of vibrationally hot CF_3CFHO radicals which decompose promptly to CF_3 + HCFO, in the more exothermic source reaction.

(k) Steady-state photolysis of F_2 in the presence of CF_3CFH_2-O_2-N_2 mixtures (p = 910 mbar) with FTIR absorption spectroscopic analysis.

(l) Steady-state photolysis of Cl_2 in the presence of CF_3CHF_2-air mixtures (1 atm) with FTIR absorption spectroscopic analysis; a 109 ± 5% yield of $C(O)F_2$ was observed, consistent with $k_1[O_2] \ll k_2$.

(m) Similar experiments to those in Comment (l) at a total pressure of 986 mbar; a $\sim$ 100% yield of $C(O)F_2$ was observed consistent with $k_1[O_2] \ll k_2$.

Preferred Values

$R_1(R_2)CHO = CF_3CHFO$
$k_1/k_2 = 4.0 \times 10^{-20}$ cm^3 molecule^{-1} at 298 K and 1 bar pressure.
$k_1/k_2 = 2.1 \times 10^{-25} \exp(3625/T)$ (1bar) cm^3 molecule^{-1} over the temperature range 260-355 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

$R_1(R_2)CHO = CF_3CHFO$
The recommended temperature dependence rate coefficient ratio is that evaluated by Wallington et al. (1996) from their own data together with those of Wallington et al. (1992), Tuazon and Atkinson (1993b), Meller et al. (1994) and Benarek et al. (1996). The data were corrected for a small pressure dependence measured by Wallington at al. (1996) at 298 K and the expression refers to reactions of the thermalised CF_3CHFO radicals. This study also revealed that energy rich CF_3CHFO radicals were formed when the radical was produced from the CF_3CHFO_2 + NO reaction, leading to formation of HC(O)F by prompt decomposition at atmospheric temperatures, reducing the relative rate of O_2 reaction by a factor of 1.8–4.0. Several theoretical studies have investigated the decomposition of CF_3CHFO radicals and have confirmed that this interpretation is realistic. (Schneider et al., 1998; Somnitz and Zellner, 2001).

$R_1(R_2)CHO$ = other radicals in the above table.
For the purpose of atmospheric modeling studies it is recommended that the above qualitative information on the ratios k_1/k_2 be used to decide if one or other of the alkoxy radical reaction pathways predominates or if both pathways should be considered.

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IV.A1.55-61

$$RO_2 + NO \rightarrow RO + NO_2 \quad (1)$$

$$RO_2 + NO + M \rightarrow RONO_2 + M \quad (2)$$

(R = CH_2F, CHF_2, CF_3, CH_2FCHF, CHF_2CF_2, CF_3CHF, CF_3CF_2)

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

Reaction Number	k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients				
IV.A1.55	R=CH_2F			
	$(1.25 \pm 0.13) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
IV.A1.56	R=CHF_2			
	$(1.26 \pm 0.16) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
IV.A1.57	R=CF_3			
	$(1.78 \pm 0.36) \times 10^{-11}$	295	Plumb and Ryan, 1982	DF-MS (b)
	$1.45 \times 10^{-11} (T/298)^{-(1.2\pm0.2)}$	230-430	Dognon et al., 1985	PLP-MS (c)
	$(1.45 \pm 0.20) \times 10^{-11}$	298		
	$(1.53 \pm 0.30) \times 10^{-11}$	290	Peeters et al., 1992	DF-MS (d)
	$(1.68 \pm 0.26) \times 10^{-11}$	295	Sehested and Nielsen, 1993	PR-AS (a)
	$(1.53 \pm 0.20) \times 10^{-11}$	297	Bevilacqua et al., 1993	F-CIMS (e)
	$(1.57 \pm 0.38) \times 10^{-11}$	298	Turnipseed et al., 1994	PLP-LIF (f)
	$(1.57 \pm 0.31) \times 10^{-11}$	293	Bhatnagar and Carr, 1994	FP-MS (g)
	$(1.76 \pm 0.35) \times 10^{-11}$	298	Bourbon et al., 1996	DF-LIF (h)
	$(1.6 \pm 0.3) \times 10^{-11}$	298	Louis et al., 1999	DF-MS (i)
IV.A1.58	R=CH_2FCHF			
	$> 8.7 \times 10^{-12}$	296	Wallington et al., 1994	PR-AS (a)
IV.A1.59	R=CHF_2CF_2			
	$> (9.7 \pm 1.3) \times 10^{-12}$	295	Sehested et al., 1993	PR-AS (a)
IV.A1.60	R=CF_3CHF			
	$(1.28 \pm 0.36) \times 10^{-11}$	298	Wallington and Nielsen, 1991	PR-AS (a)
	$(1.31 \pm 0.30) \times 10^{-11}$	324	Bhatnagar and Carr, 1995	FP-MS (j)
IV.A1.61	R=CF_3CF_2			
	$> (1.07 \pm 0.15) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
Branching Ratios				
IV.A1.57	R=CF_3			
	$k_2/k = (0.0167 \pm 0.0027)$	295	Nishida et al., 2004	P-FTIR (k)

Comments

(a) k determined from $+d[NO_2]/dt$ at a total pressure of 1 bar.

(b) k was independent of pressure over the range 2.5–6.8 mbar.

(c) No significant pressure dependence in k over the range 1.3–13 mbar was observed.

(d) Fast-flow system with molecular beam sampling MS at a total pressure of 2.7 mbar. k was derived from decay of CF_3O_2 and appearance of NO_2.

(e) k determined from decay of CF_3O_2 in the presence of NO; pressure range 1.1–2.7 mbar.

(f) Photolysis of CF_3Br in the presence of O_2 and NO at 93 mbar total pressure. k was obtained by fitting the measured CF_3O radical temporal profile, with formation through CF_3O_2 + NO and loss through CF_3O + NO.

(g) Photolysis of $(CF_3CO)_2O$ in the presence of O_2, N_2 and NO at 2.7–40 mbar total pressure. k obtained from the kinetics of CF_3O_2 removal and CF_3O formation. k was independent of pressure in the studied range.

(h) CF_3O_2 generated from F + CHF_3 reaction, with k determined from the formation kinetics of CF_3O when NO added; pressure range 1.1–4.0 mbar.

(i) CF_3O_2 generated from F + CHF_3 reaction, with k determined from the removal kinetics of CF_3O_2 when NO added; pressure range 0.9–4.0 mbar.

(j) Photolysis of Cl_2 in the presence of CF_3CH_2F, O_2, N_2 and NO at 16–33 mbar total pressure. k was obtained from the formation kinetics of NO_2. k was independent of pressure in the studied range.

(k) CF_3O_2 generated from the UV photolysis of $CF_3N_2CF_3$ in excess NO, N_2 and O_2 at 930 mbar. Branching ratio determined from the relative yields of CF_3ONO_2 and COF_2.

Preferred Values

R = CH_2F
$k = 1.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta \log k = \pm 0.3$ at 298 K.

R = CHF_2
$k = 1.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta \log k = \pm 0.3$ at 298 K.

R = CF_3
$k = 1.6 \times 10^{-11} (T/298)^{-1.2}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–430 K.
$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta n = \pm 0.5$.

R = CH_2FCHF
$k > 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

R = CHF_2CF_2
$k > 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

R = CF_3CHF
$k = 1.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta \log k = \pm 0.2$ at 298 K.

R = CF_3CF_2
$k > 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

R = CH_2F, CHF_2, CHF_2CF_2, CF_3CF_2
The preferred values are the rounded-off rate coefficients determined by Sehested et al. (1993).

R = CF_3
The preferred values are based on the temperature dependent data of Dognon et al. (1985), adjusted to fit a k_{298} value based on the determinations of Plumb and Ryan (1982), Dognon et al. (1985), Peeters et al. (1992), Sehested and Nielsen (1993), Bevilacqua et al. (1993), Turnipseed et al. (1994), Bhatnagar and Carr (1994), Bourbon et al. (1996) and Louis et al. (1999).

R = CH_2FCHF
The preferred value is the rounded-off lower limit of Wallington et al. (1994).

R = CF_3CHF
The preferred value is the rounded-off rate coefficient determined by Wallington and Nielsen (1991).

The temperature dependence expressions are given in the form favoured by Dognon et al. (1985), and subsequently adopted by others, which best describe the measured data. Comparison of the reported rate coefficients with those for the corresponding alkyl peroxy radicals, CH_3O_2 and $C_2H_5O_2$, indicates that the presence of a α-halogen substituent typically enhances k_{298} by a factor of about 1.5–2, with the reactions also possessing a similar dependence on temperature where comparison is possible. Although not so marked, it appears that additional α-halogen substituents result in further slight enhancements to k_{298}. Similarly to small alkyl peroxy radicals, the observations indicate that the reactions are dominated by the RO-forming channel (1). Dognon et al. (1985) measured quantum yields for NO_2 greater than unity for all the RO_2 radicals studied; suggesting that the RO_2 + NO reactions mainly form RO and NO_2, with additional NO_2 being produced from secondary chemistry. Nishida et al. (2004) have observed formation of a small yield 1.7 ± 0.3% of CF_3ONO_2 from the reaction of CF_3O_2 with NO, confirming the existence of channel (2) at 930 mbar pressure. This suggests that the reactions of the C_1 and C_2 halogenated RO_2 radicals will generally have minor channels forming $RONO_2$, but additional studies are required to confirm this.

References

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IV.A1.62

$$\mathbf{CF_3O_2 + NO_2 + M \rightarrow CF_3O_2NO_2 + M}$$

$\Delta H° = -105$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.7 \pm 0.8) \times 10^{-29} (T/298)^{-4.7}$ [O$_2$]	233-373	Caralp et al., 1988	PLP-MS (a)
$6.3 \times 10^{-33} \exp(2710/T)$ [N$_2$]	264-297	Mayer-Figge et al., 1996	(b)
$5.6 \times 10^{-29} (T/298)^{-9.1}$ [N$_2$]			

Comments

(a) Pulsed laser photolysis-MS study in 1-10 Torr O_2. Extrapolation with $F_c = \exp(-T/416)$, i.e., $F_c = 0.49$ at 298 K, and $k_\infty = 8.9 \times 10^{-12} (T/298)^{-0.72}$ cm^3 molecule^{-1} s^{-1} from RRKM model.

(b) From measurements of the reverse dissociation of $CF_3O_2NO_2$. Equilibrium constants $K_c = 3.80 \times 10^{27} \exp(-12140/T)$ cm^3 molecule^{-1} s^{-1} derived by combining the dissociation data with the recombination data from Caralp et al. (1988) over the falloff curve, assuming equal results for the bath gases N_2 and O_2. Extrapolation with $F_c = 0.31$ and $k_\infty = 7.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} .

Preferred Values

$k_0 = 5.6 \times 10^{-29} (T/298)^{-9}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 298 K.
$\Delta n = \pm 3$.

Comments on Preferred Values

The data by Mayer-Figge et al. (1996) are preferred because they cover a much broader part of the falloff curve and employ a more reasonable value of $F_c = 0.31$, thus allowing for a better extrapolation to the low pressure limit. Nevertheless, the rate data from Caralp et al. (1988) and Mayer-Figge et al. (1996) are identical over the range 1.3–13 mbar because both sets of data have been used for the conversion from dissociation to recombination rate coefficients.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$8.9 \times 10^{-12} (T/298)^{-0.72}$	233-373	Caralp et al., 1988	PLP-MS (a)
$7.7 \times 10^{-12} (T/298)^{-0.67}$	264-297	Mayer-Figge et al., 1996	(b)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

Preferred Values

$k_\infty = 7.7 \times 10^{-12} (T/298)^{-0.67}$ cm^3 molecule^{-1} s^{-1} over the temperature range 260-300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

See Comments on Preferred Values for k_0.

References

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Mayer-Figge, A., Zabel, F. and Becker, K.H.: J. Phys. Chem., 100, 6587, 1996.

IV.A1.63

$$\mathbf{CF_3O_2NO_2 + M \rightarrow CF_3O_2 + NO_2 + M}$$

$\Delta H^\circ = 105$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.4×10^{-5} exp(-9430/T) [N_2]	264-297	Mayer-Figge et al., 1996	(a)

Comments

(a) Preparation of $CF_3O_2NO_2$ by in situ photolysis of $CF_3I/O_2/NO_2/N_2$ mixtures in a 420 l reactor. Time dependence of $CF_3O_2NO_2$ decay monitored by IR absorption. Measurements in 3.7–1013 mbar of N_2 evaluated with $F_c = 0.31$, $N_c = 1.19$, and $k_\infty = 1.49 \times 10^{16}$ exp(-11940/T) s^{-1}. Similar results in O_2. Analysis of equilibrium constant gives $\Delta H^\circ = 102.7$ ($\pm$ 2.0) kJ mol^{-1}.

Preferred Values

$k_0 = 2.5 \times 10^{-5}$ exp(-9430/T) [N_2] s^{-1} over the temperature range 260-300 K.
$k_0 = 4.5 \times 10^{-19}$ [N_2] s^{-1} at 298 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 250$ K.

Comments on Preferred Values

The single measurement falls in line with data for related reactions. In addition, it could be evaluated theoretically leading to realistic molecular parameters. Because no unusual complications were observed, the data appear reliable. The observed part of the falloff curve could well be represented with F_c and k_∞ such as given in comment (a) for k_0.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.49×10^{16} exp(-11940/T)	264-297	Mayer-Figge et al., 1996	(a)

Comments

(a) See comment (a) for k_0.

Preferred Values

k_∞ = 1.5 × 10^{16} exp(-11940/T) s^{-1} over the temperature range 260-300 K.
k_∞ = 6.0 × 10^{-2} s^{-1} at 298 K.

Reliability

Δ log k_∞ = ± 0.3 at 298 K.
Δ (E/R) = ± 250 K.

Comments on Preferred Values

See Comments on Preferred Values for k_0. The theoretical analysis by Mayer-Figge et al. (1996) supersedes the more speculative earlier analysis by Destriau and Troe (1990). The falloff curve is constructed with the fitted F_c = 0.31 and N_c = 1.19 in good agreement with the recommendation given in the Introduction.

References

Destriau, M. and Troe, J.: Int. J. Chem. Kinet., 22, 915, 1990.
Mayer-Figge, A., Zabel, F. and Becker, K. H.: J. Phys. Chem., 100, 6587, 1996.

IV.A1.64

$$\begin{aligned} \mathbf{CH_2FO_2 + CH_2FO_2} &\rightarrow \mathbf{CH_2FOH + HC(O)F + O_2} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{CH_2FO + CH_2FO + O_2} \quad \mathbf{(2)} \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_{obs} = 3.3 \times 10^{-13} \exp[(700 \pm 100)/T]$	228-380	Dagaut et al., 1988	FP-UVA (a,b)
$k_{obs} = (3.07 \pm 0.65) \times 10^{-12}$	298		
$k_{obs} = (4.01 \pm 0.52) \times 10^{-12}$	298	Wallington et al., 1992	PR-UVA (a,c)
Branching Ratios			
$k_2/k > 0.77$	298	Wallington et al., 1992	UVP-FTIR (d)

Comments

(a) k_{obs} is based on the measured overall second-order decay of CH_2FO_2, defined by $-d[CH_2FO_2]/dt = 2k_{obs} [CH_2FO_2]^2$. As described in detail by Lesclaux (1997), HO_2 radicals formed from the subsequent chemistry of CH_2FO (formed from channel (2)) are expected to lead to secondary removal of CH_2FO_2. The true value of k is expected to fall in the range $k_{obs}/(1 + \alpha) < k < k_{obs}$, where $\alpha = k_2/k$.

(b) Flash photolysis of Cl_2 in the presence of CH_3F-O_2-N_2 mixtures at total pressures of 33–533 mbar. CH_2FO_2 radicals were monitored by UV absorption with $\sigma_{240\ nm} = (3.72 \pm 0.45) \times 10^{-18}$ cm^2 molecule^{-1}.

(c) Pulse radiolysis study of CH_3F-O_2-SF_6 mixtures at a total pressure of 1000 mbar. CH_2FO_2 radicals were monitored by UV absorption with $\sigma_{240\ nm} = (4.11 \pm 0.67) \times 10^{-18}$ cm^2 molecule^{-1}.

(d) CH_2FO_2 radicals were generated from the steady-state photolysis of Cl_2-CH_3F mixtures at 933 mbar pressure of air. The decay of CH_3F and the formation of products was monitored by FTIR spectroscopy. No CH_2FOH was observed within the detection limits of the apparatus. Significant amounts of HC(O)F were observed (86 ± 5%) and, in experiments with high conversions, CH_2FOOH was observed (11 ± 4%).

Preferred Values

$k = 2.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.5 \times 10^{-13} \exp(700/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-380 K.
$k_2/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 300$ K.
$\Delta (k_2/k) = ^{+0.0}_{-0.2}$ at 298 K.

Comments on Preferred Values

In the product study of Wallington et al. (1992) no formation of CH_2FOH was observed, showing that channel (1) is not of major importance at 298 K. The high yields of HC(O)F are also consistent with the dominance of channel (2), followed by reaction of CH_2FO with O_2 to form HC(O)F and HO_2. A product study of the $CH_2FO_2 + HO_2$ reaction (Wallington et al., 1994) has shown that only ca. 30% of that reaction produces CH_2FO_2H and O_2, with the remainder forming HC(O)F, H_2O

and O_2. The low yields of CH_2FO_2H observed by Wallington et al. (1992) are thus partially explained by this, but also suggest that HO_2 is probably removed by its self reaction in competition with reaction with CH_2FO_2.

The preferred value of k at 298 K is derived from the k_{obs} values reported by Dagaut et al. (1988) and Wallington et al. (1992), adjusted to be consistent with the re-evaluation of $\sigma_{240\,nm}$ (CH_2FO_2) = 4.03×10^{-18} cm^2 $molecule^{-1}$ by Nielsen and Wallington (1997). Similar to a procedure adopted by Lesclaux (1997) for peroxy radicals for which the self reaction rate coefficients are $\geq$ ca. 2×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, k is estimated to be $k_{obs}/(1 + 0.5(k_2/k))$, with this approximation assuming that the secondary reaction of HO_2 with CH_2FO_2 competes equally with its removal via HO_2 + HO_2. The reliability range reflects that k has been derived by this approximate procedure. The preferred value of E/R is based on the k_{obs} expression of Dagaut et al. (1988). This assumes that the above competition remains valid over the entire temperature range, consistent with the CH_2FO_2 and HO_2 self reactions, and reaction of CH_2FO_2 with HO_2 possessing similar temperature dependences.

References

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IV.A1.65

$$\begin{aligned} \mathbf{CHF_2O_2 + CHF_2O_2} &\rightarrow \mathbf{CHF_2OH + C(O)F_2 + O_2} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{CHF_2O + CHF_2O + O_2} \quad \mathbf{(2)} \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_{obs} = (5.0 \pm 0.7) \times 10^{-12}$	298	Nielsen et al., 1992	PR-UVA (a,b)
Branching Ratios			
$k_2/k \approx 1.0$	298	Nielsen et al., 1992	UVP-FTIR (c)

Comments

(a) k_{obs} is based on the measured overall second-order decay of CHF_2O_2, defined by $-d[CHF_2O_2]/dt = 2k_{obs}[CHF_2O_2]^2$. As described in detail by Lesclaux (1997), HO_2 radicals formed from the subsequent chemistry of CHF_2O (formed from channel (2)) are expected to lead to secondary removal of CHF_2O_2. The true value of k is expected to fall in the range $k_{obs}/(1 + \alpha) < k < k_{obs}$, where $\alpha = k_2/k$.

(b) Pulse radiolysis study of CH_2F_2-O_2-SF_6 mixtures at a total pressure of 1000 mbar. CHF_2O_2 radicals were monitored by UV absorption with $\sigma_{240\ nm} = (2.66 \pm 0.46) \times 10^{-18}$ cm^2 molecule^{-1}.

(c) CHF_2O_2 radicals were generated from the steady-state photolysis of Cl_2-CH_2F_2 mixtures in the presence of air at a total pressure of 933 mbar. The decay of CH_2F_2 and the formation of $C(O)F_2$ were monitored by FTIR spectroscopy. The yield of $C(O)F_2$ was 104 ± 2% of the removal of CH_2F_2.

Preferred Values

$k = (2.5–5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k \approx 1.0$ at 298 K.

Comments on Preferred Values

We have recommended a range of values for the rate coefficient at 298 K, based on the determination by Nielsen et al. (1992). The upper limit is the measured value of k_{obs} with no correction for possible secondary CHF_2O_2 removal by HO_2 radicals, and the lower limit is a factor of two less than the upper limit, corresponding to a maximum correction for the HO_2 radical reaction.

The product study in the same paper (Nielsen et al., 1992) showed that the only carbon-containing product was $C(O)F_2$, formed by the reaction $CHF_2O + O_2 \rightarrow C(O)F_2 + HO_2$, indicating that channel (2) is the predominant pathway. The absence of the product CHF_2O_2H expected from the reaction $CHF_2O_2 + HO_2 \rightarrow CHF_2O_2H + O_2$, raises several possibilities, including a slow reaction between CHF_2O_2 and HO_2 radicals or an alternative reaction pathway, such as $CHF_2O_2 + HO_2 \rightarrow C(O)F_2 + H_2O + O_2$. More information is needed on the kinetics and mechanism of the $CHF_2O_2 + HO_2$ reaction to define k and k_2/k more accurately.

References

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IV.A1.66

$CF_3O_2 + CF_3O_2 \rightarrow CF_3O + CF_3O + O_2$

ΔH° = -83.2 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1}s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.8 \pm 0.5) \times 10^{-12}$	295	Nielsen et al., 1992	PR-UVA (a)
1.8×10^{-12}	298	Maricq and Szente, 1992a	FP-UVA (b)
$(1.8 \pm 0.5) \times 10^{-12}$	297	Maricq and Szente, 1992b	FP-UVA (c)
$(1.2 \pm 0.3) \times 10^{-12}$	298	Biggs et al., 1997	DF-LIF/MS (d)
$(2.25 \pm 0.3) \times 10^{-12}$	295	Sehested et al., 1997	PR-UVA (e)

Comments

(a) Pulse radiolysis study of CHF_3-O_2-SF_6 mixtures at a total pressure of 1000 mbar. CF_3O_2 radicals were monitored by UV absorption with $\sigma_{230\,nm} = (2.06 \pm 0.40) \times 10^{-18}$ cm^2 molecule^{-1}, and an observed rate coefficient, $k_{obs} = (3.6 \pm 0.9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, was derived from the decay in absorption. Associated FTIR product studies using the photolysis of F_2-CHF_3-O_2-N_2 mixtures demonstrated quantitative formation of CF_3OOOCF_3, which was explained by the secondary reaction of CF_3O with CF_3O_2. The cited value of k is thus 0.5 k_{obs}, to take account of this secondary loss of CF_3O_2.

(b) Flash photolysis of CHF_3-F_2-O_2 mixtures with time-resolved absorption spectroscopy for the detection of CF_3O_2 radicals, with $\sigma_{210\,nm} = (4.3 \pm 0.3) \times 10^{-18}$ cm^2 molecule^{-1}. A value of $k_{obs} = (3.1 \pm 0.25) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} was determined from the time-dependence of the CF_3O_2 radical absorbance. The cited value of k was obtained from a simulation in which secondary removal of CF_3O_2 was explicitly represented.

(c) Flash photolysis of F_2 in the presence of N_2, O_2, He, and CF_3CFH_2. Secondary generation of CF_3O_2 in the system occurred by the reaction $CF_3CHFO \rightarrow CF_3 + HCOF$, followed by $CF_3 + O_2 + M \rightarrow CF_3O_2 + M$. CF_3O_2 radicals were monitored by UV absorption, and the 298 K value of $k_{obs} = 3.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, derived in the authors' previous study (Maricq and Szente, 1992a), was shown to provide a good description of the time dependence of the formation and removal of CF_3O_2. The previous value (Maricq and Szente, 1992a) of the rate coefficient for the elementary reaction, k, was therefore confirmed and assigned the cited error limits. Additional measurements suggested that k_{obs} decreases with increasing temperature.

(d) Experiments performed at pressures in the range 1.3 to 4 mbar. CF_3O_2 radicals were produced by the F + CHF_3 reaction or the F + CF_3I reaction, with subsequent addition of O_2. CF_3O_2 radicals were monitored by titration to NO_2 following reaction with excess NO, with detection of NO_2 by either LIF or MS. An observed rate coefficient, $k_{obs} = (2.0 \pm 1.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, was derived from the decay in CF_3O_2. The cited value of k was obtained from a simulation in which secondary removal of CF_3O_2 was explicitly considered.

(e) Pulse radiolysis study of CHF_3-O_2-SF_6 mixtures at a total pressure of 1000 mbar. CF_3O_2 radicals were monitored by UV absorption with $\sigma_{230\,nm} = 3.43 \times 10^{-18}$ cm^2 molecule^{-1}. The cited value of k was derived from simulation of the decay in absorption, using a chemical mechanism in which secondary removal of CF_3O_2 was explicitly represented.

Preferred Values

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

Reliability

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

Comments on Preferred Values

The reported quantitative formation of CF_3OOOCF_3 from CHF_3 oxidation, in the product study of Nielsen et al. (1992) is consistent with the self-reaction of CF_3O_2 proceeding via formation of CF_3O radicals, which react with CF_3O_2.

The five reported values of k are in reasonable accord, covering a range of approximately two. The discharge-flow determination of Biggs et al. (1997) lies at the low end of the range, and this may be indicative a pressure dependence of the reaction. Biggs et al. (1997) performed QRRK calculations, based on the reaction proceeding via a $[CF_3O_4CF_3]^*$ intermediate and estimated that the high pressure limiting k (achieved at ca. 35–70 mbar) is ca. 15% greater than their measured value, i.e. $(1.4 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The observed range in reported k values may also be reduced by re-evaluating the results of the UV absorption studies (Nielsen et al., 1992; Maricq and Szente, 1992a, b; Sehested et al., 1997) using the recommended CF_3O_2 absorption cross sections reported by Nielsen and Wallington (1997), which are somewhat lower than those applied by Maricq and Szente (1992a, b) and Sehested et al. (1997). This leads to respective revised values of k of 1.5×10^{-12} and 1.4×10^{-12} cm^3 molecule^{-1} s^{-1} in those studies, and a much improved general agreement among the reported studies. The preferred value of k is therefore based on the re-evaluations of the UV absorption studies and the estimated high pressure value of Biggs et al. (1997). Maricq and Szente (1992b) obtained limited evidence that k_{obs} possesses a weak negative temperature coefficient, but further temperature dependence studies are required to quantify this.

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Sehested, J., Møgelberg, T., Fagerstrom, K., Mahmoud, G. and Wallington, T. J.: Int. J. Chem. Kinet., 29, 673, 1997.

IV.A1.67

$$\mathbf{CF_3O_2 + CF_3CHFO_2 \rightarrow CF_3OH + CF_3COF + O_2} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow CF_3O + CF_3CHFO + O_2} \quad \mathbf{(2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8 \pm 3) \times 10^{-12}$	297	Maricq and Szente, 1992	(a)

Comments

(a) Flash photolysis of F_2 in the presence of CF_3CH_2F-O_2-N_2-He mixtures. CF_3CHFO_2 radicals were monitored by UV absorption with $\sigma_{213\,\mathrm{nm}} = (5.2 \pm 0.3) \times 10^{-18}$ cm^2 molecule^{-1}. The derived value of k listed above was obtained by modeling the decay of CF_3CFHO_2 radicals and the formation and decay of CF_3O_2 radicals.

Preferred Values

$k = 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K seems reasonable, but requires independent confirmation. Maricq and Szente (1992) assumed that the reaction proceeds entirely by channel (2) on the basis of studies of the self-reactions of CF_3O_2 and CF_3CHFO_2 radicals.

References

Maricq, M. M. and Szente, J. J.: J. Phys. Chem., 96, 10862, 1992.

IV.A1.68

$$\mathbf{CHF_2CF_2O_2 + CHF_2CF_2O_2 \rightarrow CHF_2CF_2O + CHF_2CF_2O + O_2}$$

Rate coefficient data

k/ cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
k_{obs} = (2.7 ± 0.6) × 10^{-12}	298	Nielsen et al., 1992a	PR-UVA (a)

Comments

(a) Pulse radiolysis study of CHF_2CHF_2-O_2-SF_6 mixtures at a total pressure of 1000 mbar. $CHF_2CF_2O_2$ radicals were monitored by UV absorption with σ_{230} = (3.2 ± 0.5) × 10^{-18} cm^2 molecule^{-1}. k_{obs} is based on the measured overall second-order decay in absorption at 230 nm, which was defined as $-d[CHF_2CF_2O_2]/dt = 2k_{obs}[CHF_2CF_2O_2]^2$. Product studies were also performed on the steady-state photolysis of Cl_2 in the presence of CHF_2CHF_2-air mixtures at 933 mbar total pressure. The decay of CHF_2CHF_2 and the formation of COF_2, the only carbon-containing product observed, were monitored by FTIR spectroscopy. The yield of COF_2 was 98 ± 2% relative to the decay of CHF_2CHF_2.

Preferred Values

No recommendation

Comments on Preferred Values

Although the value of k_{obs} reported by Nielsen et al. (1992a) is likely to be indicative of the magnitude of the self-reaction rate coefficient for $CHF_2CF_2O_2$, the probable formation of CHF_2O_2 and HO_2 radicals from the subsequent chemistry (see below) is expected to lead to secondary removal of $CHF_2CF_2O_2$, but also interferences in the absorption traces at 230 nm, because the spectra for all three peroxy radicals are similar. These two factors have opposing influences on k_{obs}, and it is not possible to derive k without a detailed understanding of the rates and mechanisms of the secondary processes and appropriate simulations of the system. No firm recommendation for k can currently be made.

The product study of Nielsen et al. (1992a) demonstrated approximately 100% formation of COF_2 from the oxidation of CHF_2CHF_2, consistent with exclusive formation of CHF_2CF_2O from the self-reaction of $CHF_2CF_2O_2$, followed by decomposition to form COF_2 and CHF_2. The CHF_2 radicals form CHF_2O_2 radicals, which are known (Nielsen et al., 1992b) to interact via their self-reaction, resulting in the formation of COF_2 and HO_2 from the subsequent reaction of CHF_2O with O_2. However, it is probable that CHF_2O_2 is also converted to CHF_2O via reaction with $CHF_2CF_2O_2$ in the system. HO_2 radicals, generated from $CHF_2O + O_2$, potentially also react with both $CHF_2CF_2O_2$ and CHF_2O_2, in competition with their self-reaction. The absence of the products $CHF_2CF_2O_2H$ and CHF_2O_2H, which might be formed in these reactions, raises several possibilities: the reactions of HO_2 with $CHF_2CF_2O_2$ and CHF_2O_2 may be too slow to compete with the self-reaction, or they may proceed by alternative pathways leading to COF_2 formation. More information is therefore needed on the kinetics and mechanism of the secondary reactions, in addition to further kinetics studies of the title reaction, to allow k to be defined more accurately.

References

Nielsen, O. J., Ellermann, T., Sehested, J. and Wallington, T. J.: J. Phys. Chem. 96, 10875, 1992a.
Nielsen, O. J., Ellermann, T., Bartkiewicz, E., Wallington, T. J. and Hurley, M. D.: Chem. Phys. Lett. 192, 82, 1992b.

IV.A1.69

$$\begin{aligned} \mathbf{CF_3CHFO_2 + CF_3CHFO_2} &\rightarrow \mathbf{CF_3COF + CF_3CHFOH + O_2} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{CF_3CHFO + CF_3CHFO + O_2} \quad \mathbf{(2)} \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$7.8 \times 10^{-13} \exp[(605 \pm 40)/T]$	211-372	Maricq and Szente, 1992	FP-UVA (a,b)
$(7 \pm 1.0) \times 10^{-12}$	297		
$(3.5 \pm 0.8) \times 10^{-12}$	295	Sehested et al., 1997	PR-UVA (a,c)
Branching Ratios			
$k_1/k = 0.28$	273	Wallington et al., 1992	UVP-FTIR (d)
$k_1/k = 0.16$	298		
$k_1/k = 0.05$	353		
$k_1/k = 0.055$	273	Tuazon and Atkinson, 1993	UVP-FTIR (e)
$k_1/k = 0.049$	298		
$k_1/k = 0.046$	320		

Comments

(a) k is defined by $-d[CF_3CHFO_2]/dt = 2k[CF_3CHFO_2]^2$.

(b) Flash photolysis of F_2 in the presence of N_2, O_2, He and CF_3CH_2F. CF_3CHFO_2 radicals were monitored by UV absorption with $\sigma_{240\text{ nm}} = (5.2 \pm 0.3) \times 10^{-13}$ cm^2 molecule^{-1}. The derived value of k listed above was obtained by modelling the decay curves for CF_3CFHO_2 radicals with a mechanism of 9 reactions.

(c) Pulse radiolysis study of CF_3CH_2F-O_2-SF_6 mixtures at a total pressure of 1000 mbar. CF_3O_2 radicals were monitored by UV absorption at 220 nm ($\sigma = 5.34 \times 10^{-18}$ cm^2 molecule^{-1}), 230 nm ($\sigma = 4.50 \times 10^{-18}$ cm^2 molecule^{-1}) and 240 nm ($\sigma = 3.06 \times 10^{-18}$ cm^2 molecule^{-1}). The cited value of k was derived from simulation of the decay in absorption, using a chemical mechanism in which secondary removal of CF_3CHFO_2 was explicitly represented.

(d) Steady-state photolysis of Cl_2 in the presence of CF_3CFH_2-O_2 mixtures at a total pressure of 933 mbar with FTIR analysis of the products HC(O)F and $CF_3C(O)F$. The branching ratio was determined from the yields of $CF_3C(O)F$ as a function of added O_2, extrapolated to zero O_2 partial pressure.

(e) Similar experiments to those of Comment (d). The branching ratios were derived from the yields of $CF_3C(O)F$ in the presence of 787 mbar N_2 and 1.3 mbar O_2.

Preferred Values

$k = 4.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.2 \times 10^{-13} \exp(605/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210-375 K.
$k_2/k = 0.90$, independent of temperature over the range 270-350 K.
$k_1/k = 0.10$, independent of temperature over the range 270-350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 200$ K.
$\Delta (k_1/k) = \Delta (k_2/k) = \pm 0.05$ over the temperature range 270-350 K.

Comments on Preferred Values

The preferred value of k at 298 K is the average of the results of Maricq and Szente (1992) (based on their Arrhenius expression) and Sehested et al. (1997). The preferred Arrhenius expression for k is based on the E/R value from the study of Maricq and Szente (1992), combined with a pre-exponential factor adjusted to give the preferred value of k at 298 K. The temperature dependence reported by Maricq and Szente (1992), is based on temperature-independent branching ratios k_1/k and k_2/k over the range 273–363 K. This is consistent with our recommendation of a temperature-independent branching ratio, k_1/k, which is the average of the experimental results of Wallington et al. (1992) and Tuazon and Atkinson (1993) over the range 273–353 K. The recommended value of k_2/k is inferred from that of k_1/k. It should be noted, however, that the results of Maricq and Szente (1992) for k at 216 K are not consistent with temperature-independent branching ratios.

The kinetics studies (Maricq and Szente, 1992; Sehested et al., 1997) report values of k at 298 K which differ by a factor of 1.7, and this is reflected in the assigned reliability range. Confirmation of both the overall rate coefficient and the branching ratios is required.

References

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IV.A1.70

$CF_3CF_2O_2 + CF_3CF_2O_2 \rightarrow CF_3CF_2O + CF_3CF_2O + O_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_{obs} = (2.10 \pm 0.38) \times 10^{-12}$	295	Sehested et al., 1993	PR-UVA (a)

Comments

(a) Pulse radiolysis study of CF_3CHF_2-O_2-SF_6 mixtures at a total pressure of 1000 mbar. $CF_3CF_2O_2$ radicals were monitored by UV absorption with $\sigma_{230\,nm} = (2.74 \pm 0.46) \times 10^{-18}$ cm^2 molecule^{-1}. k_{obs} is based on the measured overall second-order decay in absorption at 230 nm, which was defined as $-d[CF_3CF_2O_2]/dt = 2k_{obs}[CF_3CF_2O_2]^2$. Products studies were also performed on the steady-state photolysis of Cl_2 in the presence of CF_3CHF_2-air mixtures at 933 mbar total pressure. The decay of CF_3CHF_2 and the formation of products were monitored by FTIR spectroscopy. The observed products were $C(O)F_2$, $CF_3O_3CF_3$ and $CF_3O_3C_2F_5$, and accounted for 100% of the CF_3CF_2H loss.

Preferred Values

No recommendation

Comments on Preferred Values

Although the value of k_{obs} reported by Sehested et al. (1993) is likely to be indicative of the magnitude of the self-reaction rate coefficient for $CF_3CF_2O_2$, the formation of CF_3O_2 and CF_3O radicals from the subsequent chemistry (see below) leads to secondary removal of $CF_3CF_2O_2$, but also interferences in the absorption traces at 230 nm, because the spectra for $CF_3CF_2O_2$ and CF_3O_2 are almost identical. These two factors have opposing influences on k_{obs}, and it is not possible to derive k without a detailed understanding of the rates and mechanisms of the secondary processes and appropriate simulations of the system. No firm recommendation for k can currently be made.

The quantitative formation of $C(O)F_2$ observed in the product study of Sehested et al. (1993) is consistent with exclusive formation of CF_3CF_2O from the self-reaction of $CF_3CF_2O_2$, followed by decomposition to form $C(O)F_2$ and CF_3. The CF_3 radicals form CF_3O_2 radicals, which are known (Nielsen et al., 1992) to interact via their self-reaction, resulting in the formation of CF_3O. However, it is probable that CF_3O_2 is also converted to CF_3O via reaction with $CF_3CF_2O_2$ in the system. Further removal of both $CF_3CF_2O_2$ and CF_3O_2 occurs via their reactions with CF_3O, which lead to the observed products $CF_3O_3C_2F_5$ and $CF_3O_3CF_3$ (Sehested et al., 1993). More information is therefore needed on the kinetics and mechanism of the secondary reactions, in addition to further kinetics studies of the title reaction, to allow k to be defined more accurately.

References

Nielsen, O. J., Ellermann, T., Sehested, J., Bartkiewiecz, E., Wallington, T. J. and Hurley, M. D.: Int. J. Chem. Kinet., 24, 1009, 1992.

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IV.A1.71

$HC(O)F + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			$\Delta H°$/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$HC(O)F + h\nu$	$\rightarrow HF + CO$	(1)	8.7	13,730
	$\rightarrow H + FCO$	(2)	458	261
	$\rightarrow F + HCO$	(3)	515	232

Absorption cross-section data

Wavelength range/nm	References	Comments
200-340	Rattigan et al., 1994	(a)
200–370	Meller and Moortgat, 1992	(b)

Comments

(a) The absorption spectrum of HC(O)F was studied using a purified sample of HC(O)F and recorded by diode array spectroscopy with a resolution of 1.2 nm. The characteristic banded structure was recorded and the absolute cross-section at 230 nm was $\sigma = 6.65 \times 10^{-20}$ cm^2 molecule^{-1} using this resolution. The cross-section was independent of temperature in the range 233–318 K, in agreement with the earlier work of Giddings and Innes (1961).

(b) Measurements of the spectrum of HC(O)F at a resolution of 0.02 nm. The spectrum consists of a vibrational progression of many sharp bands, with an origin of structured absorption at 268 nm and a maximum of intensity near 210 nm. The maximum value of $\sigma = 1.5 \times 10^{-19}$ cm^2 molecule^{-1} was observed at this resolution, which is in reasonable agreement with the earlier work of Giddings and Innes (1961) who reported an absorption coefficient of approximately 501 mol^{-1} cm^{-1} ($\sigma = 1.9 \times 10^{-19}$ cm^2 molecule^{-1}) at the maximum.

Quantum Yield Data

There are no reported quantum yield data. Klimeck and Berry (1973) have observed infrared laser emission from HF* following flash photolysis of HC(O)F ($\lambda >$165 nm), indicating the occurrence of reactions (1) and/or (3). Reed et al. (1997) and Maul et al., (1999) have used H-atom photofragment translational spectroscopy in a pulsed molecular beam to study H atoms formed by channel (2) at $\sim$ 243-247 nm.

Preferred Values

Absorption cross-sections for HC(O)F at 298 K

λnm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2
200	8.28	223	6.58	245	0.67
201	9.75	224	4.94	246	0.72
202	8.3	225	5.33	247	0.41
203	7.55	226	4.00	248	0.48
204	8.52	227	4.65	249	0.28
205	10.15	228	4.43	250	0.21
206	8.28	229	4.61	251	0.15
207	7.41	230	3.57	252	0.24
208	8.44	231	2.55	253	0.21
209	9.55	232	3.16	254	0.07
210	7.76	233	3.09	255	0.12
211	7.36	234	2.98	256	0.07
212	7.92	235	2.04	257	0.05
213	8.56	236	2.28	258	0.04
214	9.22	237	1.24	259	0.04
215	7.67	238	1.71	260	0.04
216	6.51	239	1.75	261	0.02
217	7.38	240	1.55	262	0.02
218	7.97	241	0.97	263	0.02
219	6.28	242	1.19	264	0.02
220	6.85	243	0.57	265	0.01
221	5.7	244	0.76	266	0.01
222	6.07				

Quantum Yields for HC(O)F

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data for the absolute absorption cross-sections reported by Meller and Moortgat (1992). The listed values are averaged over 1 nm. The cross-sections of Rattigan et al. (1994) are higher than those of Meller and Moortgat (1992) by approximately a factor of 2 at 230 nm. Although the two studies are nominally at comparable resolution, the Rattigan et al. (1994) spectrum does not appear to contain all the features reported by Meller and Moortgat (1992), indicating possible errors.

References

Giddings, L. K. and Innes, K. K.: J. Molecular Spectr. 6, 528, 1961.
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Maul, C., Dietrich, C., Haas, T., Gericke, K. -H., Tachikawa, H., Langford, S. R., Kono, M., Reed, D. L., Dixon, R. N. and Ashfold, M. N. R. : Phys. Chem. Chem. Phys., 1, 767, 1999.
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Rattigan, O. V., Rowley, D. M., Wild, O., Jones, R. L. and Cox, R. A.: J. Chem. Soc. Faraday Trans., 90, 1818, 1994.
Reed, C. K., Kono, M., Langford, S. R., Hancock, T. W. R., Dixon, R. N. and Ashfold, M. N. R.: J. Chem. Phys., 106, 6198, 1997.

IV.A1.72

$C(O)F_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$C(O)F_2 + h\nu$	$\rightarrow FCO + F$	(1)	562	213
	$\rightarrow CO + 2F$	(2)	683	175
	$\rightarrow CF_2 + O(^3P)$	(3)	700	171

Quantum yield data

Measurement	Wavelength range/nm	References	Comments
$\Phi_1 = 0.94 \pm 0.06$	193	Nölle et al., 1992, 1999	(a)
$\Phi_1 = 0.58 \pm 0.05$	210	Nölle et al., 1999	(b)
$\Phi_1 = 0.57 \pm 0.05$	210		(b,c)
$\Phi_1 = 0.07 \pm 0.03$	220		(b)
$\Phi_1 = 0.11 \pm 0.02$	220		(b,c)

Comments

(a) Laser photolysis at 296-298 K with initial $C(O)F_2$ pressures of 10-30 mbar. Because of the high concentrations of FCO radicals in the laser photolysis experiments, formation of $C(O)F_2$ was assumed to occur via the reaction $FCO + FCO \rightarrow C(O)F_2 + CO$ as observed in analogous experiments with C(O)FCl (Nölle et al., 1999). Therefore, the cited quantum yield is the measured value (0.47 ± 0.03) corrected for reformation of $C(O)F_2$ from the FCO radical self-reaction.

(b) Photolysis at 298K using a medium pressure mercury lamp-monochromator combination, with initial $C(O)F_2$ pressures of 2.1–6.3 mbar. Because of the low concentrations of FCO radicals in these experiments, reformation of $C(O)F_2$ from the reaction $FCO + FCO \rightarrow C(O)F_2 + CO$ was not anticipated to be significant, as confirmed by observations in analogous experiments with C(O)FCl (Nölle et al., 1999). Therefore, the cited quantum yield is the measured value.

(c) With added N_2 diluent gas at pressures of 600–1000 mbar.

Preferred Values

Absorption cross-sections for $C(O)F_2$ photolysis at 298 K

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2
186.0	5.5	205.1	0.74
187.8	4.8	207.3	0.52
189.6	4.2	209.4	0.40
191.4	3.7	211.6	0.28
193.2	3.1	213.9	0.20
195.1	2.6	216.2	0.12
197.0	2.1	218.6	0.081
199.0	1.6	221.0	0.049
201.0	1.3	223.5	0.035
203.0	0.95	226.0	0.024
		228.6	0.018

Quantum Yields for $C(O)F_2$ Photolysis at 298 K

$\Phi_1 = 0.94$ at 193 nm
$\Phi_1 = 0.57$ at 210 nm
$\Phi_1 = 0.09$ at 220 nm

Comments on Preferred Values

The preferred values of the absorption cross sections are those reported by Molina and Molina (1982) over the wavelength range 184–199 nm and by Nölle et al. (1992) at longer wavelengths. The results of these two studies are in excellent agreement over the range 200–208 nm; from 208–225 nm the results of Molina and Molina (1982) are 15–25% smaller than those of Nölle et al. (1992). The spectrum shows considerable structure; the values listed are averages over 500 cm^{-1} intervals. Nölle et al. (1992; 1999) photolyzed $C(O)F_2$ at three wavelengths in the range 193–220 nm. The overall quantum yield for loss of $C(O)F_2$, which must be through channel (1), decreases monotonically with increasing wavelength. In the absence of confirmatory data, the quantum yields measurd by Nölle et al. (1992; 1999) are recommended.

References

Molina, L. T. and Molina, M. J.: Results presented at the 182nd American Chemical Society National Meeting, New York, August 1982.
Nölle, A., Heydtmann, H., Meller, R., Schneider, W. and Moortgat, G. K.: Geophys. Res. Lett. 19, 281, 1992.
Nölle, A., Krumscheid, C. and Heydtmann, H.: Chem. Phys. Lett. 299, 561, 1999.

IV.A1.73

$CF_3CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$CF_3CHO + h\nu$	$\rightarrow CF_3 + HCO$	(1)		
	$\rightarrow CF_3CO + H$	(2)		
	$\rightarrow CHF_3 + CO$	(3)		

Absorption cross-section data

Wavelength range/nm	References	Comments
230-360	Meller et al., 1993	(a)
200–400	Sellevȧg et al., 2004	(b)

Quantum yield data

Measurement	Wavelength range/nm	References	Comments
$\Phi_1 < 0.02$	290-400	Sellevȧg et al., 2004	(c)

Comments

(a) Absolute absorption cross-sections were measured using a diode-array spectrometer over the temperature range 240–300 K. The UV spectrum of trifluoroacetaldehyde shows a broad band, centered at 305 nm and extending out to 355 nm. Values of σ were given at 5 nm intervals at 298 K.

(b) Absolute absorption cross-sections were measured using a diode-array spectrometer over the temperature range 298±2 K, at a spectral resolution of 2 nm. The UV spectrum of trifluoroacetaldehyde shows a broad band, centered at ~300 nm and extending out to ≥355 nm. Values of σ were given at 5 nm intervals at 298 K.

(c) Photolysis of CF_3CHO in pure air in the presence of an HO radical tracer (di-*n*-butyl ether) in the ~200 m^3 EUPHORE chamber facility under natural sunlight conditions. The measured first-order loss rate of CF_3CHO during a ~3 hr period around solar noon was 7.74×10^{-6} s^{-1}, essentially identical to the leak obtained from monitoring the decay of SF_6. After correction for the leak rate and reaction with HO radicals, the calculated first-order loss rate of CF_3CHO due to photolysis during this ~3 hr period was $<8.5 \times 10^{-7}$ s^{-1}, compared to the calculated photolysis rate of 5.5×10^{-5} s^{-1} using a unit quantum yield for photodissociation.

Preferred Values

Absorption cross-sections of CF_3CHO at 298 K

λ/nm	10^{21} σ/cm^2	λ/nm	10^{21} σ/cm^2
200	2.38	305	31.3
205	2.22	310	29.2
210	1.97	315	26.5
215	1.52	320	22.5
220	1.05	325	19.0
225	0.76	330	14.4
230	0.78	335	10.6
235	0.74	300	29.8
240	1.29	305	29.0
245	2.17	310	27.9
250	3.44	315	25.0
255	5.25	320	21.4
260	7.63	325	17.7
265	10.6	330	13.6
270	13.8	335	9.98
275	17.6	340	6.17
280	21.3	345	3.86
285	24.8	350	2.31
290	27.6	355	0.59
295	29.1	360	0.19
300	31.7		

Quantum Yields of CF_3CHO

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data reported by Sellevȧg et al. (2004), which are $\sim$7% higher than the data of Meller et al. (1993) at the peak absorpion at $\sim$300 nm and within the combined experimental uncertainties. No recommendation is made for the quantum yields but by analogy with other aldehydes, which show a similar absorption spectrum, any photodissociation at wavelengths $>$ 300 nm is expected to be predominantly by channel (1). The only data concerning quantum yields are those of Sellevȧg et al. (2004) for irradiation by natural sunlight at 290–400 nm, with an average photodissociation quantum yield of $<$0.02 for this wavelength region.

The products of photolysis of CF_3CHO have been investigated by Dodd and Watson-Smith (1957). More recently, Richer et al. (1993) have studied the photooxidation of CF_3CHO and observed CHF_3, CO, CO_2 and COF_2 as products. Photodissociation appears to occur predominantly via reaction (1). However, Richer et al. (1993) observed substantial yields (14%) of CHF_3 in the 254 nm photolysis of CF_3CHO in air, indicating that channel (3) also occurs at that wavelength.

References

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IV.A1.74

$CF_3C(O)F + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$CF_3C(O)F + h\nu$	$\rightarrow CF_3 + CFO$	(1)		
	$\rightarrow CF_3CO + F$	(2)		

Absorption cross-section data

Wavelength range/nm	References	Comments
200–300	Rattigan et al., 1993	(a)
210–265	Meller et al., 1993	(b)

Quantum yield data

Measurement	Wavelength range/nm	References	Comments
$\Phi_1 + \Phi_2 = 1.05 \pm 0.05$	254	Meller et al., 1993	(c)
$\Phi_1 + \Phi_2 = 1.02 \pm 0.05$	240	Bierbrauer et al., 1999	(d)

Comments

(a) Absolute absorption cross sections were measured using a dual-beam diode array spectrometer over the temperature range 240-300 K. The UV spectrum of trifluoroacetyl fluoride shows a single band extending out to 300 nm, where there is significant temperature dependance, Values of σ were given at 5 nm intervals at 293 K and 238 K as well as temperature coefficients in the long wavelength tail at $\lambda > 270$nm.

(b) Absolute absorption cross sections were measured using a dual-beam diode array spectrometer at 298K. Cross sections were averaged over 1, 2 and 5 nm wavelength intervals.

(c) Average of 10 measurements of the overall loss of $CF_3C(O)F$ by photolysis in 1 atm air at 298 K, relative to the loss of $C(O)Cl_2$, for which $\Phi = 1$.

(d) Measurement of the overall loss of $CF_3C(O)F$ in the presence of O_2 (0.67-6.7 mbar) at 298 K.

Preferred Values

Absorption cross-sections of $CF_3C(O)F$ at 293K and 238 K

λ/nm	10^{20} σ/cm^2 293K	10^{20} σ/cm^2 238K	10^3 B/K^{-1a}
200	9.35	9.46	-0.21
205	11.50	11.60	-0.16
210	12.88	13.10	-0.31
215	13.72	13.70	0.03
220	13.39	13.10	0.40
225	11.93	11.40	0.83
230	9.75	9.11	1.23
235	7.26	6.55	1.87
240	4.93	4.18	2.99
245	3.01	2.30	4.91
250	1.67	1.16	6.60
255	0.82	0.49	9.36
260	0.35	0.18	12.40
265	0.13	0.05	18.77
270	0.04	0.01	26.36
275	0.012	0.003	24.73
280	0.004	0.001	23.32
285	0.0016	0.0004	25.21
290	0.0008	0.00	
295	0.0003	0.00	

[a] $\ln \sigma(T) = \ln \sigma(293\text{ K}) + B(T\text{-}293)$.

Quantum Yields of $CF_3C(O)F$ at 298 K

$\Phi_1 + \Phi_2 = 1.0$ over the wavelength range 200–300 nm.

Comments on Preferred Values

The preferred values for the cross-sections at 293 K are a simple average of the data reported by Rattigan et al. (1993) and Meller et al. (1993). The temperature dependence is based on the 238 K data of Rattigan et al. (1993). The quantum yield of unity is based on the data of Meller et al. (1993) and of Bierbrauer et al. (1999), and is assumed to apply over the wavelength region 200–300 nm.

References

Bierbrauer, K. L., Chiappero, M. S., Malanca, F. E. and Argüllo, G. A.: J. Photobiol. A: Chem., 122, 73, 1999.
Meller, R., Boglu, D. and Moortgat, G. K.: ”Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere,” STEP-HALOCSIDE/AFEAS Workshop, Dublin, Eire, March 23-25, pp. 130-138, 1993.
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Appendix 2: ClO_x Reactions

IV.A2.75

$$\begin{array}{lll} \mathbf{O(^1D) + CHF_2Cl} & \rightarrow \mathbf{O(^3P) + CHF_2Cl} & \mathbf{(1)} \\ & \rightarrow \mathbf{ClO + CHF_2} & \mathbf{(2)} \\ & \rightarrow \textbf{other products} & \mathbf{(3)} \end{array}$$

$\Delta H°(1) = -190\ kJ \cdot mol^{-1}$
$\Delta H°(2) = -92\ kJ \cdot mol^{-1}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(0.95 \pm 0.3) \times 10^{-10}$	173-343	Davidson et al., 1978	PLP (a)
$(1.08 \pm 0.20) \times 10^{-10}$	298	Warren et al., 1991	PLP-RF
Branching Ratios			
$k_1/k = 0.28 \pm 0.06$	298	Warren et al., 1991	PLP-RF (b)
$k_2/k = 0.55 \pm 0.10$	298	Addison et al., 1979	PLP-UVA (c)

Comments

(a) Pulsed laser photolysis of O_3 at 266 nm. $O(^1D)$ atoms were monitored by time-resolved emission at 630 nm.

(b) Branching ratio was determined from the ratio of the $O(^3P)$ yield from $O(^1D) + CHF_2Cl$ relative to that for $O(^1D) + N_2$.

(c) Quantitative yields of ClO were determined via the (5,0) band of the $A^2\pi \leftarrow X^2\pi$ system.

Preferred Values

$k = 1.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} independent of temperature over the range 170-350 K.
$k_1/k = 0.28$ at 298 K.
$k_2/k = 0.55$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ over the temperature range 170-350 K.
$\Delta (k_1/k) = \pm 0.1$ at 298 K.
$\Delta (k_2/k) = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred value of k is based on the results of Davidson et al. (1978) and the room temperature value of Warren et al. (1991). The preferred value of the branching ratio k_1/k is the value reported by Warren et al. (1991). The preferred value of the branching ratio k_2/k is the value reported by Addison et al. (1979).

References

Addison, M. C., Donovan, R. J. and Garraway, J.: J. Chem. Soc. Faraday Discuss., 67, 286, 1979.
Davidson, J. A., Schiff, H. I., Brown, T. J. and Howard, C. J.: J. Chem. Phys., 69, 4277, 1978.
Warren, R., Gierczak, T. and Ravishankara, A. R.: Chem. Phys. Lett., 183, 403, 1991.

IV.A2.76

$$\mathbf{O(^1D) + CHFCl_2 \rightarrow ClO + CHFCl \quad (1)}$$
$$\mathbf{\rightarrow other\ products \quad (2)}$$

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

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.9 \pm 0.6) \times 10^{-10}$	188-343	Davidson et al., 1978	PLP (a)
Branching Ratios			
$k_1/k= 0.74 \pm 0.15$	298	Takahashi et al., 1996	PLP-LIF (b)

Comments

(a) Pulsed laser photolysis of O_3 at 266 nm. $O(^1D)$ atoms were monitored by time-resolved emission at 630 nm.

(b) Branching ratio for ClO formation was determined by measurement of the LIF signal intensity of ClO normalized to that from $O(^1D)$ + HCl.

Preferred Values

$k = 1.9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} independent of temperature over the range 180-350 K.
k_1/k = 0.74 at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ over the temperature range 180–350 K.
$\Delta (k_1/k) = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred value of k is based on the results of Davidson et al. (1978). The preferred value of the branching ratio k_1/k is based on the results of Takahashi et al. (1996).

References

Davidson, J. A., Schiff, H. I., Brown, T. J. and Howard, C. J.: J. Chem. Phys., 69, 4277, 1978.
Takahashi, K., Wada, R., Matsumi, Y. and Kawasaki, M.: J. Phys. Chem., 100, 10145, 1996.

IV.A2.77

$$\begin{aligned} \mathbf{O(^1D) + CH_3CF_2Cl} &\rightarrow \mathbf{O(^3P) + CH_3CF_2Cl} \quad &\mathbf{(1)} \\ &\rightarrow \textbf{other products} \quad &\mathbf{(2)} \end{aligned}$$

$\Delta H°(1) = -190\ \mathrm{kJ{\cdot}mol^{-1}}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.15 \pm 0.20) \times 10^{-10}$	298	Warren et al., 1991	PLP-RF
Branching Ratios			
$k_1/k = 0.26 \pm 0.05$	298	Warren et al., 1991	PLP-RF (a)

Comments

(a) Branching ratio was determined from the ratio of the $O(^3P)$ yield from $O(^1D) + CH_3CF_2Cl$ relative to that for $O(^1D) + N_2$.

Preferred Values

$k = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.26$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value of k and the preferred value of the branching ratio k_1/k are based on the results of Warren etal. (1991). In these experiments, only $O(^3P)$ was monitored and therefore no direct information relating to the products of the chemical reaction of $O(^1D) + CH_3CF_2Cl$ was obtained.

References

Warren, R., Gierczak, T. and Ravishankara, A. R.: Chem. Phys. Lett., 183, 403, 1991.

IV.A2.78

$$\mathbf{O(^1D) + CH_3CFCl_2 \rightarrow O(^3P) + CH_3CFCl_2 \quad (1)}$$
$$\mathbf{\rightarrow \text{other products} \quad (2)}$$

$\Delta H^\circ(1)$ = -190 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.58 \pm 0.20) \times 10^{-10}$	298	Warren et al., 1991	PLP-RF
Branching Ratios			
$k_1/k = 0.31 \pm 0.05$	298	Warren et al., 1991	PLP-RF (a)

Comments

(a) Branching ratio was determined from the ratio of the O(^{3}P) yield from O(^{1}D) + CH_3CFCl_2 relative to that for O(^{1}D) + N_2.

Preferred Values

$k = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.31$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value of k and the preferred value of the branching ratio k_1/k are based on the results of Warren et al. (1991), the only published study of this reaction. In these experiments, only O(^{3}P) was monitored and therefore no direct information relating to the products of the chemical reaction of O(^{1}D) + CH_3CFCl_2 was obtained.

References

Warren, R., Gierczak, T. and Ravishankara, A. R.: Chem. Phys. Lett., 183, 403, 1991.

IV.A2.79

$$\begin{array}{llr} \mathbf{O(^1D) + CH_2ClCF_3} & \mathbf{\rightarrow O(^3P) + CH_2ClCF_3} & \mathbf{(1)} \\ & \mathbf{\rightarrow \text{other products}} & \mathbf{(2)} \end{array}$$

$\Delta H°(1)$ = -190 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.20 \pm 0.06) \times 10^{-10}$	298	Warren et al., 1991	PLP-RF
Branching Ratios			
$k_1/k = 0.20 \pm 0.05$	298	Warren et al., 1991	PLP-RF (a)

Comments

(a) Branching ratio was determined from the ratio of the O(^{3}P) yield from O(^{1}D) + CH_2ClCF_3 relative to that for O(^{1}D) + N_2.

Preferred Values

$k = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.20$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value of k and the preferred value of the branching ratio k_1/k are based on the results of Warren et al. (1991). In these experiments, only O(^{3}P) was monitored and therefore no direct information relating to the products of the chemical reaction of O(^{1}D) + CH_2ClCF_3 was obtained.

References

Warren, R., Gierczak, T. and Ravishankara, A. R.: Chem. Phys. Lett., 183, 403, 1991.

IV.A2.80

$$\mathbf{O(^1D) + CH_2ClCF_2Cl \rightarrow O(^3P) + CH_2ClCF_2Cl \quad (1)}$$
$$\mathbf{\rightarrow \text{other products} \quad (2)}$$

$\Delta H°(1) = -190$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_2 = (1.6 \pm 0.6) \times 10^{-10}$	297	Green and Wayne, 1976	RR (a)

Comments

(a) O(^{1}D) produced by photolysis of NO_2 at 229 nm. $\Delta(CH_2ClCF_2Cl)/\Delta(N_2O)$ monitored by IR absorption spectroscopy. Measured rate coefficient ratio of $k_2/k(O(^1D) + N_2O) = 1.4 \pm 0.3$ is placed on an absolute basis by use of $k(O(^1D) + N_2O) = 1.16 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current evaluation). The cited rate coefficient refers to chemical reaction only and does not include physical quenching.

Preferred Values

$k_2 = 1.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value of k_2 is derived from the relative rate results reported by Green and Wayne (1976) in the only published study of this reaction. It should be noted that this rate coefficient refers to chemical reaction only and does not include physical quenching of O(^{1}D).

References

Green, R. G. and Wayne, R. P.: J. Photochem., 6, 371, 1976.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.

IV.A2.81

$$\begin{aligned} \mathbf{O(^1D) + CHFClCF_3} &\rightarrow \mathbf{O(^3P) + CHFClCF_3} \quad &\mathbf{(1)} \\ &\rightarrow \mathbf{other\ products} \quad &\mathbf{(2)} \end{aligned}$$

$\Delta H°(1) = -190$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.6 \pm 0.4) \times 10^{-11}$	298	Warren et al., 1991	PLP-RF
Branching Ratios			
$k_1/k = 0.31 \pm 0.10$	298	Warren et al., 1991	PLP-RF (a)

Comments

(a) Branching ratio was determined from the ratio of the O(^{3}P) yield from O(^{1}D) + $CHFClCF_3$ relative to that for O(^{1}D) + N_2.

Preferred Values

$k = 8.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.31$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred value of k and the preferred value of the branching ratio k_1/k are based on the results of Warren et al. (1991), the only published study of this reaction. In these experiments, only O(^{3}P) was monitored and therefore no direct information relating to the products of the chemical reaction of O(^{1}D) + $CHFClCF_3$ was obtained.

References

Warren, R., Gierczak, T. and Ravishankara, A. R.: Chem. Phys. Lett., 183, 403, 1991.

IV.A2.82

$$\mathbf{O(^1D) + CHCl_2CF_3 \rightarrow O(^3P) + CHCl_2CF_3 \quad (1)}$$
$$\mathbf{\rightarrow \text{other products} \quad (2)}$$

$\Delta H°(1) = -190$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.98 \pm 0.15) \times 10^{-10}$	298	Warren et al., 1991	PLP-RF
Branching Ratios			
$k_1/k = 0.21 \pm 0.08$	298	Warren et al., 1991	PLP-RF (a)

Comments

(a) Branching ratio was determined from the ratio of the O(^{3}P) yield from O(^{1}D) + $CHCl_2CF_3$ relative to that for O(^{1}D) + N_2.

Preferred Values

$k = 2.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.21$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred value of k and the preferred value of the branching ratio k_1/k are based on the results of Warren et al. (1991). In these experiments, only O(^{3}P) was monitored and therefore no direct information relating to the products of the chemical reaction of O(^{1}D) + $CHCl_2CF_3$ was obtained.

References

Warren, R., Gierczak, T. and Ravishankara, A. R.: Chem. Phys. Lett.,183, 403, 1991.

IV.A2.83

$$\begin{aligned} \mathbf{O(^1D) + CF_2Cl_2} &\rightarrow \mathbf{ClO + CF_2Cl} \quad &\mathbf{(1)} \\ &\rightarrow \mathbf{O(^3P) + CF_2Cl_2} \quad &\mathbf{(2)} \end{aligned}$$

$\Delta H°(1)$ = -123 kJ·mol^{-1}
$\Delta H°(2)$ = -190 kJ·mol^{-1}

Rate coefficient data (k = k_1 + k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.45 \pm 0.5) \times 10^{-10}$	173-343	Davidson et al., 1978	PLP (a)
$(1.4 \pm 0.2) \times 10^{-10}$	298	Force and Wiesenfeld, 1981	PLP-RA
Branching Ratios			
$k_2/k = 0.14 \pm 0.07$	298	Force and Wiesenfeld, 1981	PLP-RA (b)
$k_1/k = 0.87 \pm 0.18$	298	Takahashi et al., 1996	PLP-LIF (c)
$k_2/k = 0.19 \pm 0.05$	298	Takahashi et al., 1996	PLP-LIF (d)

Comments

(a) Pulsed laser photolysis of O_3 at 266 nm. O(^{1}D) atoms were monitored by time-resolved emission at 630 nm.

(b) O(^{1}D) atoms were monitored by resonance absorption at 130.4 nm and compared to O(^{3}P) atoms in the presence of ozone in He diluent where the O(^{3}P) atom yield from the O(^{1}D) + O_3 reaction is 1.0.

(c) Branching ratio for ClO formation was determined by measurement of the LIF signal intensity of ClO normalized to that from O(^{1}D) + HCl.

(d) Branching ratio for quenching of O(^{1}D) to O(^{3}P) was determined by comparison of the VUV-LIF signal intensity for CF_2Cl_2 with that of N_2.

Preferred Values

$k = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} independent of temperature over the range 170–350 K.
k_1/k = 0.83 at 298 K.
k_2/k = 0.17 at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ over the temperature range 170–350 K.
$\Delta (k_1/k) = \pm 0.17$ at 298 K.
$\Delta (k_2/k) = \pm 0.17$ at 298 K.

Comments on Preferred Values

The preferred value of k is based on the results of Davidson et al. (1978) and the room temperature result of Force and Wiesenfeld (1981). The preferred value of the branching ratio k_2/k is the average of the values reported by Force and Wiesenfeld (1981) and by Takahashi et al. (1996). The preferred value of the branching ratio k_1/k was derived from the value reported by Takahashi et al. (1996), adjusted to make the sum of the two preferred branching ratios equal to unity.

References

Davidson, J. A., Schiff, H. I., Brown, T. J. and Howard, C. J.: J. Chem. Phys., 69, 4277, 1978.
Force, A. P. and Wiesenfeld, J. R.: J. Phys. Chem., 85, 782, 1981.
Takahashi, K., Wada, R., Matsumi, Y. and Kawasaki, M.: J. Phys. Chem., 100, 10145, 1996.

IV.A2.84

$$\mathbf{O(^1D) + CFCl_3} \quad \rightarrow \mathbf{ClO + CFCl_2} \quad \mathbf{(1)}$$
$$\rightarrow \mathbf{O(^3P) + CFCl_3} \quad \mathbf{(2)}$$

$\Delta H°(1) = -142\ \mathrm{kJ{\cdot}mol^{-1}}$
$\Delta H°(2) = -190\ \mathrm{kJ{\cdot}mol^{-1}}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.7) \times 10^{-10}$	173-343	Davidson et al., 1978	PLP (a)
$(2.4 \pm 0.2) \times 10^{-10}$	298	Force and Wiesenfeld, 1981	PLP-RA
Branching Ratios			
$k_2/k = 0.13 \pm 0.05$	298	Force and Wiesenfeld, 1981	PLP-RA (b)
$k_1/k = 0.88 \pm 0.18$	298	Takahashi et al., 1996	PLP-LIF (c)

Comments

(a) Pulsed laser photolysis of O_3 at 266 nm. $O(^1D)$ atoms were monitored by time-resolved emission at 630 nm.

(b) $O(^1D)$ atoms were monitored by resonance absorption at 130.4 nm and compared to $O(^3P)$ atoms in the presence of ozone in He diluent where the $O(^3P)$ atom yield from the $O(^1D) + O_3$ reaction is 1.0.

(c) Branching ratio for ClO formation was determined by measurement of the LIF signal intensity of ClO normalized to that from $O(^1D)$ + HCl.

Preferred Values

$k = 2.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} independent of temperature over the range 170–350 K.
$k_1/k = 0.87$ at 298 K.
$k_2/k = 0.13$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ over the temperature range 170–350 K.
$\Delta (k_1/k) = \pm 0.13$ at 298 K.
$\Delta (k_2/k) = \pm 0.13$ at 298 K.

Comments on Preferred Values

The preferred value of k is based on the results of Davidson et al. (1978) and the room temperature result of Force and Wiesenfeld (1981). The preferred value of the branching ratio k_2/k is the value reported by Force and Wiesenfeld (1981). The preferred value of the branching ratio k_1/k was derived from the value reported by Takahashi et al. (1996), adjusted to make the sum of the two preferred branching ratios equal to unity.

References

Davidson, J. A., Schiff, H. I., Brown, T. J. and Howard, C. J.: J. Chem. Phys., 69, 4277, 1978.
Force, A. P. and Wiesenfeld, J. R.: J. Phys. Chem., 85, 782, 1981.
Takahashi, K., Wada, R., Matsumi, Y. and Kawasaki, M.: J. Phys. Chem., 100, 10145, 1996.

IV.A2.85

$$\begin{aligned} \mathbf{O(^1D) + CCl_4} &\rightarrow \mathbf{ClO + CCl_3} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{O(^3P) + CCl_4} \quad \mathbf{(2)} \end{aligned}$$

$\Delta H°(1)$ = -170 kJ·mol^{-1}
$\Delta H°(2)$ = -190 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.1 \pm 0.9) \times 10^{-10}$	203-343	Davidson et al., 1978	PLP (a)
$(3.5 \pm 0.3) \times 10^{-10}$	298	Force and Wiesenfeld, 1981	PLP-RA
Branching Ratios			
$k_2/k = 0.14 \pm 0.06$	298	Force and Wiesenfeld, 1981	PLP-RA (b)
$k_1/k = 0.90 \pm 0.19$	298	Takahashi et al., 1996	PLP-LIF (c)

Comments

(a) Pulsed laser photolysis of O_3 at 266 nm. $O(^1D)$ atoms were monitored by time-resolved emission at 630 nm.

(b) $O(^1D)$ atoms were monitored by resonance absorption at 130.4 nm and compared to $O(^3P)$ atoms in the presence of ozone in He diluent where the $O(^3P)$ atom yield from the $O(^1D) + O_3$ reaction is 1.0.

(c) Branching ratio for ClO formation was determined by measurement of the LIF signal intensity of ClO normalized to that from $O(^1D)$ + HCl.

Preferred Values

$k = 3.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} independent of temperature over the range 200–350 K.
$k_1/k = 0.88$ at 298 K.
$k_2/k = 0.12$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ over the temperature range 200–350 K.
$\Delta (k_1/k) = \pm 0.12$ at 298 K.
$\Delta (k_2/k) = \pm 0.12$ at 298 K.

Comments on Preferred Values

The preferred value of k is based on the results of Davidson et al. (1978) and the room temperature result of Force and Wiesenfeld (1981). The preferred values of the branching ratios were derived from the values reported by Force and Wiesenfeld (1981) (k_2/k) and by Takahashi et al. (1996) (k_1/k), with both reported values being reduced slightly to make the sum of the two preferred branching ratios equal to unity.

References

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Takahashi, K., Wada, R., Matsumi, Y. and Kawasaki, M.: J. Phys. Chem., 100, 10145, 1996.

IV.A2.86

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

ΔH° (1) = -190 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.7 \pm 0.4) \times 10^{-10}$	298	Fletcher and Husain, 1978	FP-RA (a)

Comments

(a) Flow system used, with $O(^1D)$ atoms being monitored by time-resolved resonance absorption at 115 nm. The data analysis used a modified Beer-Lambert law.

Preferred Values

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

Reliability

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

Comments on Preferred Values

The preferred value is derived from the data of Fletcher and Husain (1978) by use of a scaling factor of 0.5. The weight of evidence from many $O(^1D)$ rate studies suggests that $O(^1D)$ rates reported by Husain and co-workers contain a systematic error, and that these results can be made consistent with other $O(^1D)$ recommended values in this evaluation by use of this scaling factor, as has been done in previous evaluations by the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry and by the NASA Panel for Data Evaluation. See also the discussion of this topic in Davidson et al. (1978).

References

Davidson, J. A., Schiff, H. I., Brown, T. J. and Howard, C. J.: J. Chem. Phys., 69, 4277, 1978.
Fletcher, I. S. and Husain, D.: J. Photochem. 8, 355, 1978.

IV.A2.87

$$\mathbf{O(^1D) + COCl_2 \rightarrow O(^3P) + COCl_2 \quad (1)}$$
$$\mathbf{\rightarrow O(^3P) + Cl_2 + CO \quad (2)}$$
$$\mathbf{\rightarrow \text{other products} \quad (3)}$$

$\Delta H°(1)$ = -190 kJ·mol^{-1}
$\Delta H°(2)$ = -80 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.6 \pm 0.5) \times 10^{-10}$	298	Chichinin, 1997	PLP-LMR
$2.04 \times 10^{-10} \exp[(27 \pm 10)/T]$	194-429	Strekowski et al., 2000	PLP-RF
$(2.22 \pm 0.33) \times 10^{-10}$	298		
Branching Ratios			
$(k_1 + k_2)/k = 0.20 \pm 0.04$	194-429	Strekowski et al., 2000	PLP-RF (a)

Comments

(a) Branching ratio for conversion of O(^{1}D) to O(^{3}P), i.e. $(k_1 + k_2)/k$ was determined by comparison of the O(^{3}P) yield from O(^{1}D) + $COCl_2$ relative to that for O(^{1}D) + N_2.

Preferred Values

$k = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.0 \times 10^{-10} \exp(25/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 190-430 K.
$(k_1 + k_2)/k = 0.20$.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 25$ K.
$\Delta (k_1 + k_2)/k = \pm 0.10$

Comments on Preferred Values

The preferred values of k are based on the results reported by Strekowski et al. (2000). The room temperature value reported by Chichinin et al. (1997) is 17% higher than the preferred value. The branching ratio $(k_1 + k_2)/k$ is taken from Strekowski et al. (2000). Jayanty et al. (1976) present evidence, based on high yields of CO, that the reaction channel to produce ClO + ClCO is very important.

References

Chichinin, A. I.: J. Chem. Phys. 106, 1057, 1997.
Jayanty, R. K. M., Simonaitis, R. and Heicklen, J.: J. Photochem., 5, 217, 1976.
Strekowski, R. S., Nicovich, J. M. and Wine, P. H.: Chem. Phys. Lett. 330, 354, 2000.

IV.A2.88

$Cl + HC(O)Cl \rightarrow HCl + ClCO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
7.9×10^{-13}	305	Sanhueza and Heicklen, 1975	RR (a)
$(7.7 \pm 1.0) \times 10^{-13}$	298 ± 2	Niki et al., 1980	RR (b)
8.3×10^{-12} exp(-705/T)	266-321	Libuda et al., 1990	RR (c)
7.8×10^{-13}	298		
7.8×10^{-12} exp(-720/T)	222-296	Orlando, 1999	RR (d)
7.0×10^{-13}	298		

Comments

(a) Rate coefficient ratios of k(Cl + HC(O)Cl)/k(Cl + CH_3Cl) = 1.85 ± 0.43 and k(Cl + HC(O)Cl)/k(Cl + CH_2Cl_2) = 1.66 ± 0.15 derived from the kinetic analysis of HC(O)Cl in Cl atom-sensitized oxidation of CH_2Cl_2 and CH_3Cl. This was placed on an absolute basis by use of k(Cl + CH_3Cl) = 5.3×10^{-13} cm^3 molecule^{-1} s^{-1} and k(Cl + CH_2Cl_2) = 3.6×10^{-13} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation). The rate coefficient cited in the table is the average of the two values obtained, which however differ significantly.

(b) Rate coefficient ratio of k(Cl + HC(O)Cl)/k(Cl + CH_3Cl) = 1.6 ± 0.2 determined using FTIR absorption spectroscopy in irradiated Cl_2-CH_3Cl-O_2-N_2 mixtures at 933 mbar total pressure. The rate coefficient ratio was placed on an absolute basis by use of k(Cl + CH_3Cl) = 4.8×10^{-13} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) Relative rate study. Cl atoms generated by the photolysis of Cl_2 in Cl_2-HC(O)Cl-CH_4-N_2 mixtures at 1000 mbar total pressure. The concentrations of HC(O)Cl and CH_4 were measured by FTIR absorption spectroscopy (HC(O)Cl) and/or gas chromatography (CH_4). Rate coefficient ratios were determined over the temperature range 265.8–321.3 K, and placed on an absolute basis by use of k(Cl + CH_4) = 6.6×10^{-12} exp(-1240/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(d) Temperature dependent rate coefficient ratios of k(Cl + HC(O)Cl)/k(Cl + CH_2Cl_2) were derived from the kinetic analysis of HC(O)Cl in Cl atom-sensitized oxidation of CH_2Cl_2. Placed on an absolute basis by use of k(Cl + CH_2Cl_2) = 5.9×10^{-12} exp(-850/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation). The value of k at 298 K was taken from the Arrhenius expression presented.

Preferred Values

$k = 7.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.1 \times 10^{-12}$ exp(-710/T) cm^3 molecule^{-1} s^{-1} over the temperature range 220-330 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 150$ K.

Comments on Preferred Values

At 298 K, the rate coefficients of Niki et al. (1980), Libuda et al. (1990), and Orlando (1999) are in good agreement, and form the basis of the recommendation at this temperature. The results of Sanhueza and Heicklen (1975) are also consistent with this value. The recommended temperature dependence is based on the studies of Libuda et al. (1990) and Orlando (1999), which are in excellent agreement. The A-factor has been adjusted to reproduce the recommended value of k at 298 K.

References

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Libuda, H. G., Zabel, F., Fink, E. H. and Becker, K. H.: J. Phys. Chem., 94, 5860, 1990.
Niki, H., Maker, P. D., Savage, C. M. and Breitenbach, L. P.: Int. J. Chem. Kinet., 12, 915, 1980.
Orlando, J. J.: Int. J. Chem. Kinet., 31, 515, 1999.
Sanhueza, E. and Heicklen, J.: J. Phys. Chem., 79, 7, 1975.

IV.A2.89

$$\mathbf{Cl + CH_3OCl \rightarrow Cl_2 + CH_3O \quad (1)}$$
$$\mathbf{\rightarrow HCl + CH_2OCl \quad (2)}$$

$\Delta H°(1) = -39.7$ kJ·mol^{-1}
$\Delta H°(2) = -14.2$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.0 \pm 0.2) \times 10^{-11}$	300	Kukui et al., 1997	DF-MS/LIF (a)
Relative Rate Coefficients			
$(6.3 \pm 0.1) \times 10^{-11}$	295	Carl et al., 1996	RR (b)
Branching Ratios			
$k_1/k = 0.8 \pm 0.2$	295	Carl et al., 1996	(c)
$k_2/k = 0.2 \pm 0.1$	295		
$k_1/k = 0.85 \pm 0.06$	300	Kukui et al., 1997	DF-MS/LIF (a)

Comments

(a) Flow tube operated at 2.5 – 3.5 mbar of He. Cl and Cl_2 monitored as their parent ions, CH_3O was monitored by LIF, but not quantified. The relative sensitivity of the MS to Cl and Cl_2 was determined by titration of Cl to Cl_2 via reaction with NOCl. Rate coefficients were obtained from the Cl decay in excess CH_3OCl, and the branching ratio, k_1/k, was derived by numerical modeling of Cl loss and Cl_2 production processes both in the desired reaction and secondary processes.

(b) Relative rates of removal of CH_3OCl and C_2H_6 (reference reactant) monitored by FTIR in air and N_2 bath gas at total pressure of 133 to 988 mbar. The value $k/k(Cl + C_2H_6) = 1.07 \pm 0.02$ was combined with the IUPAC (2007) recommendation for $k(Cl + C_2H_6)$ to yield the value for k listed in the table.

(c) Branching ratios determined by quantitative analysis of CH_3OCl loss combined with HCl formation (FTIR experiments) and also by CH_3OCl loss combined with Cl_2 formation (UV experiments). The chemistry was initiated by photolysis of Cl_2 or CH_3OCl itself. The HCl formation was modeled to assess the effects of secondary reactions such as Cl + HCHO.

Preferred Values

$k = 6.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.85$ at 298 K.
$k_2/k = 0.15$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (k_1/k) = \pm 0.1$ at 298 K.
$\Delta (k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred values of k(298 K) is an average of the absolute and relative rate experiments, which are in excellent agreement. A consistent result for the branching ratios also emerges from these studies, and the value obtained by Kukui et al. (1997) for

k_1/k is adopted. The product analysis of Carl et al. (1996) provides confirmation of this result, and that channel (2) provides the rest of the product formation. Theoretical work confirms the existence of these two reaction channels, and suggests comparable effciencies at room temperature and dominance of hydrogen abstraction at higher temperatures (He et al., 2005).

References

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IV.A2.90

$$\mathbf{Cl + CH_3F \rightarrow HCl + CH_2F}$$

ΔH° = -12.8 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.1 \times 10^{-12} \exp[-(790 \pm 45)/T]$	216-296	Manning and Kurylo, 1977	FP-RF (a)
3.6×10^{-13}	298		
$(2.7 \pm 0.2) \times 10^{-13}$	298	Hitsuda et al., 2001	PLP-LIF (b)
Relative Rate Coefficients			
$1.3 \times 10^{-11} \exp(-1050/T)$	273-368	Tschuikow-Roux et al., 1988	RR (c)
3.8×10^{-13}	298		
$(3.4 \pm 0.7) \times 10^{-13}$	298	Tuazon et al., 1992	RR (d)
$(3.24 \pm 0.51) \times 10^{-13}$	298	Wallington et al., 1992	RR (e)

Comments

(a) Cl atoms were formed by the photolysis of CCl_4. The Arrhenius expression was derived by least squares fitting to tabulated data, excluding those in which CH_3F was excited by CO_2 laser.

(b) Laser photolysis of HCl at 193 nm as Cl atom source. Both Cl($^2P_{3/2}$) and Cl($^2P_{1/2}$) were detected by VUV-LIF.

(c) Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC. Derived values of A/A_{CH4} = (2.02 ± 0.01) and $(E\text{-}E_{CH4})/R$ = (-190 ± 6) K are placed on an absolute basis using k(Cl + CH_4) = $6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(d) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FT-IR spectroscopy. The measured rate coefficient was placed on absolute basis by use of k(Cl + CH_4) = 1.0×10^{-13} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(e) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by IR absorption. The measured rate coefficient was placed on an absolute basis by use of a rate coefficient of k(Cl + CH_4) = 1.0×10^{-13} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 3.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.0 \times 10^{-12} \exp(-730/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240-370 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

The recommended value at 298 K is based on an average of all the data at this temperature excepting that of Hitsuda et al. (2001) which is lower than the others. The recommended expression for k is derived by least squares fitting to the temperature dependent data set of Manning and Kurylo (1977), which covers the atmospherically most relevant temperature range, and the room temperature data of Tuazon et al. (1992) and Wallington et al. (1992). The rate coefficients of Tschuikow-Roux et al. (1988) show good agreement in the common temperature range but a slightly greater temperature dependence. A steeper temperature dependence at high temperatures has also been observed in an unpublished experimental study covering 200 to 700 K, which was reported in the theoretical study of Rosenman and McKee (1997).

References

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Tuazon, E. C., Atkinson, R. and Corchnoy, S. B.: Int. J. Chem. Kinet., 24, 639, 1992.
Wallington, T. J., Ball, J. C., Nielsen, O. J. and Bartkiewicz, E.: J. Phys. Chem,. 96, 1241, 1992.

IV.A2.91

$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$

ΔH° = -14.3 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.1 \times 10^{-10} \exp[(-1790 \pm 70)/T]$	300-604	Clyne and Walker, 1973	DF-MS
5.4×10^{-13}	300		
$3.4 \times 10^{-11} \exp[(-1250 \pm 60)/T]$	233-322	Manning and Kurylo, 1977	FP-RF
$(5.10 \pm 0.14) \times 10^{-13}$	296		
$(4.4 \pm 0.6) \times 10^{-13}$	298	Beichert et al., 1995	DF-RF
$4.0 \times 10^{-14}\, T^{0.92} \exp(-795/T)$	300-843	Bryukov et al., 2002	DF-MS
$(5.2 \pm 0.3) \times 10^{-13}$	300		
Relative Rate Coefficients			
$(4.8 \pm 0.4) \times 10^{-13}$	295 ± 2	Wallington et al., 1990	RR (a)
$(4.7 \pm 0.6) \times 10^{-13}$	298	Beichert et al., 1995	RR (b)
$1.0 \times 10^{-11} \exp[-(915 \pm 120)/T]$	222-298	Orlando, 1999	RR (c)
4.7×10^{-13}	298		

Comments

(a) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-CH_3Cl-CH_4 air mixtures at 930 mbar total pressure. The concentrations of CH_3Cl and CH_4 were monitored by FTIR absorption spectroscopy and a rate coefficient ratio $k(Cl + CH_3Cl)/k(Cl+CH_4) = 4.79 \pm 0.39$ determined. This was placed on an absolute basis by use of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-CH_3Cl-CH_4 mixtures at atmospheric pressure of N_2, air or Ar. The concentrations of CH_3Cl and CH_4 were monitored by GC and a rate coefficient ratio $k(Cl + CH_3Cl)/k(Cl+CH_4) = 4.65 \pm 0.57$ was determined. This was placed on an absolute basis by use of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-CH_3Cl-CH_4 mixtures at 930 mbar total pressure of O_2-N_2. The concentrations of CH_3Cl and CH_4 were monitored by FTIR absorption spectroscopy and a temperature dependent rate coefficient ratio $k(Cl + CH_3Cl)/k(Cl+CH_4)$ determined. This was placed on an absolute basis by use of $k(Cl + CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation). The results were consistent with those obtained using CH_3Br as reference reactant.

Preferred Values

$k = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.3 \times 10^{-11} \exp(-1150/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-360 K.

Reliability

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

Comments on Preferred Values

The results of all studies are in reasonable agreement at room temperature and below, though the data sets of Clyne and Walker (1973) and Bryukov et al. (2002) diverge significantly at higher temperatures. The preferred 298 K rate coefficient is the average of all studies at room temperature, excepting that of Clyne and Walker (1973). The temperature dependence was derived by least squares fitting to the data of Manning and Kurylo (1977), Orlando (1999) and Bryukov et al. (2002) at temperatures below 360 K where these data sets are in very good agreement.

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IV.A2.92

$Cl + CH_2F_2 \rightarrow HCl + CHF_2$

ΔH° = 0.5 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
1.0×10^{-11} exp(-1470/T)	281-368	Tschuikow-Roux et al., 1985	RR (a)
7.3×10^{-14}	298		
$(3.2 \pm 0.2) \times 10^{-14}$	295	Nielsen et al., 1992	RR (b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC. Derived values of A/A_{CH4}= (1.51 ± 0.06) and $(E\text{-}E_{CH4})/R$ = (228 ± 12) K were placed on an absolute basis using $k(Cl + CH_4) = 6.6 \times 10^{-12}$ exp(-1240/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) Photolysis of Cl_2 in presence of CH_2F_2 and CH_4 in 920 mbar air or N_2 bath gas. The value obtained, $k/CH_2F_2)/k(CH_4)$ = 0.32 ± 0.02 was placed on an absolute value using $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 5.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.0 \times 10^{-12}$ exp(-1470/T) cm^3 molecule^{-1} s^{-1} over the temperature range 280-370 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The recommended value at 298 K is an average of the two studies reported above. The temperature dependence is based on the study of Tschuikow-Roux et al. (1985), with the A-factor adjusted to reproduce the recommended value of k at 298 K. The large error limits in k and E/R reflect the poor agreement between these studies.

References

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IV.A2.93

$Cl + CH_2FCl \rightarrow HCl + CHFCl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$1.2 \times 10^{-11} \exp(-1230/T)$	273-368	Tschuikow-Roux et al., 1988	RR (a)
1.9×10^{-13}	298		
$(1.10 \pm 0.25) \times 10^{-13}$	298	Tuazon et al., 1992	RR (b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC, and the measured rate coefficient ratio was placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 9.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) Cl atoms were generated by photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.0 \times 10^{-12} \exp(-1230/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270-370 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The recommended value is based on the room temperature results of Tuazon et al. (1992) and the temperature dependence reported by Tschuikow-Roux et al. (1988).

References

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Tuazon, E. C., Atkinson, R. and Corchnoy, S. B.: Int. J. Chem. Kinet., 24, 639, 1992.

IV.A2.94

$Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$

$\Delta H° = -19.9\ kJ\cdot mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.5 \pm 0.5) \times 10^{-13}$	298	Davis et al., 1970	FP-RF
$8.6 \times 10^{-11} \exp[-(1450 \pm 60)/T]$	298-621	Clyne and Walker, 1973	DF-MS
6.4×10^{-13}	298		
$(3.2 \pm 0.2) \times 10^{-13}$	298	Beichert et al., 1995	DF-RF
$1.48 \times 10^{-16}\ T^{1.58} \exp(-360)/T)$	296-790	Bryukov et al., 2002	DF-RF
$(3.5 \pm 0.2) \times 10^{-13}$	297		
Relative Rate Coefficients			
$(3.65 \pm 0.39) \times 10^{-13}$	298	Niki et al., 1980	RR (a)
$1.9 \times 10^{-11} \exp(-1190)/T)$	273-368	Tschuikow-Roux et al., 1988	RR (b)
3.5×10^{-13}	298		
$(3.45 \pm 0.18) \times 10^{-13}$	298	Beichert et al., 1995	RR (c)
$(3.51 \pm 0.14) \times 10^{-13}$	298	Catoire et al., 1996	RR (d)
$4.4 \times 10^{-12} \exp(-770)/T)$	222-298	Orlando, 1999	RR (e)
3.2×10^{-13}			

Comments

(a) Relative to Cl + CH_3Cl. Cl atoms were generated by the photolysis of Cl_2 in the presence of CH_2Cl_2 and CH_3Cl in air at 930 mbar and the concentrations of CH_2Cl_2 and CH_4 measured by FTIR. The measured rate coefficient ratio of $k(Cl + CH_2Cl_2)/k(Cl + CH_3Cl) = (0.76 \pm 0.08)$ was placed on an absolute basis using $k(Cl + CH_3Cl) = 4.8 \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ (IUPAC, current recommendation).

(b) Cl atoms were generated by the photolysis of Cl_2 at 424 nm, and the concentrations of CH_2Cl_2 and CH_3Cl measured by GC. The measured rate coefficient ratio of $k(Cl + CH_2Cl_2)/k(Cl + CH_4) = (2.81 \pm 0.02) \exp[-(49 \pm 2)/T]$ is placed on an absolute basis by using the rate coefficient of $k(Cl + CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)\ cm^3\ molecule^{-1}\ s^{-1}$ (IUPAC, current recommendation).

(c) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-CH_2Cl_2-CH_4 mixtures at atmospheric pressure of N_2, air or Ar. The concentrations of CH_3Cl and CH_4 were monitored by GC and a rate coefficient ratio $k(Cl + CH_2Cl_2)/k(Cl+CH_4) = 3.45 \pm 0.18$ was determined. This was placed on an absolute basis by use of $k(Cl + CH_4) = 1.0 \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ (IUPAC, current recommendation).

(d) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-CH_2Cl_2-CH_4 in air at 930 mbar total pressure. The relative removal rates of CH_2Cl_2 and CH_4 were measured by FTIR. A rate coefficient ratio $k(Cl + CH_2Cl_2)/k(Cl+CH_4) = 3.51 \pm 0.14$ was obtained and placed on an absolute basis by use of $k(Cl + CH_4) = 1.0 \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ (IUPAC, current recommendation).

(e) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-CH_3Cl-CH_4 mixtures at 930 mbar total pressure of O_2-N_2. The concentrations of CH_3Cl and CH_4 were monitored by FTIR absorption spectroscopy and a temperature dependent rate coefficient ratio $k(Cl + CH_2Cl_2)/k(Cl+CH_4)$ determined. This was placed on an absolute basis by use of $k(Cl + CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)\ cm^3\ molecule^{-1}\ s^{-1}$ (IUPAC, current recommendation). The results were consistent with those obtained using CH_3Br as reference reactant.

Preferred Values

$k = 3.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.9 \times 10^{-12}$ exp(-850/T) cm^3 molecule^{-1} s^{-1} over the temperature range 220-400 K.

Reliability

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

Comments on Preferred Values

With the exception of the results of Davis et al. (1970) and Clyne and Walker (1973), the remaining 7 studies at room temperature are consistent with a value of $(3.4 \pm 0.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Note, that for reaction with CH_4, both the room temperature rate coefficients of Davis et al. (1970) and Clyne and Walker (1973) and the temperature dependence of Clyne and Walker (1973) are higher than recommended values, indicating possible systematic errors in these studies. The temperature dependent rate coefficients of Orlando (1999) and Bryukov et al. (2002) are in good agreement at temperatures less than ≈ 400 K. The preferred temperature dependence is taken from a least squares fit to these two data sets between 400 and 220 K, and has been adjusted to reproduce the recommended value of k at 298 K. Curvature in the Arrhenius plot makes extrapolation beyond this temperature range problematic, hence use of the 3-parameter fit of Bryukov et al. (2002) to cover temperatures up to 800 K.

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IV.A2.95

$$\mathbf{Cl + CHF_2Cl \rightarrow HCl + CF_2Cl}$$

ΔH° = -9.0 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.7 \pm 0.2) \times 10^{-15}$	297	Sawerysyn et al., 1992	DF-MS
$5.3 \times 10^{-12} \exp[-(2430 \pm 90)/T]$	298-430	Talhaoui et al., 1996	DF-MS
$(1.4 \pm 0.3) \times 10^{-15}$	296		
Relative Rate Coefficients			
$(2.0 \pm 0.4) \times 10^{-15}$	298	Tuazon, et al., 1992	RR (a)

Comments

(a) Cl atoms were generated by photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient was placed on an absolute basis by use of a rate coefficient of k(Cl + CH_4) = 1.0×10^{-13} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.9 \times 10^{-12} \exp(-2430/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290-430 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred value at 298 K is based on the absolute study of Talhaoui et al. (1996) and the relative rate measurement of Tuazon et al. (1992), which are in reasonable agreement. The work of Talhaoui et al. (1996) is assumed to supersede that of Sawerysyn et al. (1992). The recommended temperature dependence is based on the results of Talhaoui et al. (1996), with expanded error limits to reflect the fact that this is the only study of k(T). The A-factor has been adjusted to reproduce the value of k at 298 K.

References

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IV.A2.96

$Cl + CHFCl_2 \rightarrow HCl + CFCl_2$

ΔH° = -17.8 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
5.2×10^{-12} exp[-(1675 ± 60)/T]	298-430	Talhaoui et al., 1996	DF-MS
$(1.9 \pm 0.3) \times 10^{-14}$	296		
Relative Rate Coefficients			
$(1.0 \pm 0.2) \times 10^{-14}$	294	Glavas and Heicklen, 1985	RR (a)
$(2.1 \pm 0.4) \times 10^{-14}$	298	Tuazon et al., 1992	RR (b)

Comments

(a) Steady-state photolysis of Cl_2-$CHFCl_2$-O_2-NO-NO_2-N_2 mixtures. The measured rate coefficient ratio is placed on absolute basis by use of a rate coefficient of k(Cl + NO + M) = 1.0×10^{-31} cm^6 molecule^{-2} s^{-1}.

(a) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient was placed on absolute basis by use of a rate coefficient of k(Cl + CH_4) = 1.0×10^{-13} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 2.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.5 \times 10^{-12}$ exp(-1675/T) cm^3 molecule^{-1} s^{-1} over the temperature range 290-430 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred value at 298 K is based on the absolute study of Talhaoui et al. (1996) and the relative rate study of Tuazon et al. (1992). These results are preferred over the earlier, less direct results of Glavas and Heicklen (1985). The recommended temperature dependence is based on the results of Talhaoui et al. (1996), with expanded error limits to reflect the fact that this is the only study of k(T). The A-factor has been adjusted to reproduce the recommended value of k at 298 K.

References

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IV.A2.97

$Cl + CHCl_3 \rightarrow HCl + CCl_3$

ΔH° = -39.2 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.45 \times 10^{-11} \exp[-(1379 \pm 44)/T]$	297-652	Clyne and Walker, 1973	DF-MS
$(1.47 \pm 0.35) \times 10^{-13}$	297		
$(3.7 \pm 1.0) \times 10^{-13}$	298	Jeoung et al., 1991	(a)
$(1.1 \pm 0.1) \times 10^{-13}$	298	Beichert et al., 1995	DF-RF
$8.0 \times 10^{-12} \exp[-(1390 \pm 80)/T]$	298-430	Talhaoui et al., 1996	DF-MS
$(7.6 \pm 1.3) \times 10^{-14}$	298		
$1.19 \times 10^{-16}\ T^{1.51} \exp(-571/T)$	297-854	Bryukov et al., 2002	DF-RF
$(8.9 \pm 0.9) \times 10^{-14}$	297		
Relative Rate Coefficients			
$1.9 \times 10^{-12} \exp(-980/T)$	286-593	Knox, 1962	RR (b,c)
6.9×10^{-14}	298		
$6.0 \times 10^{-12} \exp(-1283/T)$	240-593	Knox, 1962	RR (b,d)
8.1×10^{-14}	298		
$(1.13 \pm 0.07) \times 10^{-13}$	298	Beichert et al., 1995	RR (e)
$(1.19 \pm 0.13) \times 10^{-13}$	298	Brahan et al., 1996	RR (f)
$(1.1 \pm 0.1) \times 10^{-13}$	298	Catoire et al., 1996	RR (g)
$2.5 \times 10^{-12} \exp(-915/T)$	222-298	Orlando, 1999	RR (h)
1.15×10^{-13}	298		

Comments

(a) Very low pressure reactor with chemiluminescence and mass spectrometric detection. The reaction of Cl with $CHCl_3$ was studied as part of a complex chemical system.

(b) Cl atoms were generated by photolysis of Cl_2 in Cl_2-$CHCl_3$-CH_4 or Cl_2-$CHCl_3$-CH_3Cl mixtures. Organic reactants and products monitored by GC.

(c) Rate coefficient ratio of $k(Cl + CHCl_3)/k(Cl + CH_4) = 0.286 \exp(259/T)$ was obtained and placed on an absolute basis by use of $k(Cl + CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(d) Rate coefficient ratio of $k(Cl + CHCl_3)/k(Cl + CH_3Cl) = 0.26 \exp(-133/T)$ obtained, and placed on an absolute basis by use of $k(Cl + CH_3Cl) = 2.3 \times 10^{-11} \exp(-1150/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(e) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-$CHCl_3$-CH_4 mixtures at atmospheric pressure of N_2, air or Ar. The concentrations of $CHCl_3$ and CH_4 were monitored by GC and a rate coefficient ratio $k(Cl + CHCl_3)/k(Cl+CH_4) = 1.13 \pm 0.07$ was determined. This was placed on an absolute basis by use of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(f) Cl atoms were generated by photolysis of Cl_2 in Cl_2-$CHCl_3$-CH_4 or Cl_2-$CHCl_3$-CH_3Cl mixtures in an air or N_2 bath gas at 1023 mbar total pressure and 298 K. Rate coefficient ratios $k(Cl + CHCl_3)/k(Cl+CH_4)$ and $k(Cl + CHCl_3)/k(Cl+CH_3Cl)$ were placed on an absolute basis by use of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $k(Cl + CH_4) = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}(IUPAC, current recommendation). The value presented in the table is the average of experiments using both CH_4 and CH_3Cl as reference reactants.

(g) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-$CHCl_3$-CH_4 mixtures at 930 mbar total pressure of air. The relative removal rates of CH_2Cl_2 and CH_4 were measured by FTIR. A rate coefficient ratio $k(Cl + CHCl_3)/k(Cl+CH_4)$ = 1.1 ± 0.1 was obtained and placed on an absolute basis by use of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, current recommendation).

(h) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-$CHCl_3$-CH_4 mixtures at 930 mbar total pressure of O_2-N_2. The concentrations of $CHCl_3$ and CH_4 were monitored by FTIR absorption spectroscopy and a temperature dependent rate coefficient ratio $k(Cl + CHCl_3)/k(Cl+CH_4)$ determined. This was placed on an absolute basis by use of $k(Cl + CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, current recommendation). The results were consistent with those obtained using CH_3Br as reference reactant

Preferred Values

$k = 1.1 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 2.4 \times 10^{-12} \exp(-920/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 220-500 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

The absolute rate constants of Beichert et al. (1995) and Bryukov et al. (2002), and the relative rate constants of Beichert et al. (1995), Brahan et al. (1996), Catoire et al. (1996) and Orlando (1999) are in good agreement. The 298 K recommendation is an average result from these studies. The temperature dependent data of Orlando (1999) and Bryukov et al. (2002) are reasonably well described by the expression for 220 K< T < 500 K given above, which has been adjusted to give the recommended value of k at 298 K. For extrapolation to higher temperatures, an expression of the form $k = AT^n \exp(E/RT)$ as given by Bryukov et al (2002) is suitable.

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IV.A2.98

$$\begin{aligned} \mathbf{Cl + CH_3CH_2F} &\rightarrow \mathbf{HCl + CH_3CHF} \quad &\mathbf{(1)} \\ &\rightarrow \mathbf{HCl + CH_2CH_2F} \quad &\mathbf{(2)} \end{aligned}$$

$\Delta H°(1)$ = -9.6 kJ·mol^{-1}
$\Delta H°(2)$ = -5.3 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.8 \pm 0.5) \times 10^{-12}$	298	Hitsuda et al., 2001	PLP-LIF (a)
Relative Rate Coefficients			
$k_1 = 1.0 \times 10^{-11}$ exp(-130/T)	281-368	Tschuikow-Roux et al., 1985	RR (b)
$k_1 = 6.5 \times 10^{-12}$	298		
$k_2 = 8.3 \times 10^{-12}$ exp(-720/T)	281-368		
$k_2 = 7.4 \times 10^{-13}$	298		

Comments

(a) Laser photolysis of HCl at 193 nm as Cl atom source. Both Cl($^2P_{3/2}$) and Cl($^2P_{3/2}$) detected by VUV-LIF.

(b) Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC and the measured rate coefficient ratios were placed on an absolute basis by use of a rate coefficient of k(Cl + CH_4) = 6.6 × 10^{-12} exp(-1240/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k_1 = 6.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 1.0 \times 10^{-11}$ exp(-130/T) cm^3 molecule^{-1} s^{-1} over the temperature range 280-370 K.
$k_2 = 7.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 8.3 \times 10^{-12}$ exp(-720/T) cm^3 molecule^{-1} s^{-1} over the temperature range 280-370 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.3$ at 298 K.
$\Delta (E_1/R) = \Delta (E_2/R) = \pm 500$ K.

Comments on Preferred Values

The recommended values are based on the results of the relative rate study of Tschuikow-Roux et al. (1985). The overall rate constant k at room temperature, ($k = k_1 + k_2$), of Hitsuda et al. (2001) is consistent with this recommendation.

References

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IV.A2.99

$$\mathbf{Cl + CH_3CHF_2 \rightarrow HCl + CH_3CF_2 \quad (1)}$$
$$\mathbf{\rightarrow HCl + CH_2CHF_2 \quad (2)}$$

$\Delta H°(1) = -4.9$ kJ·mol^{-1}
$\Delta H°(2) = 11.1$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$k_1 = 7.0 \times 10^{-12} \exp(-965/T)$	280-360	Yano and Tschuikow-Roux, 1986	RR (a)
$k_1 = 2.7 \times 10^{-13}$	298		
$k_2 = 7.8 \times 10^{-12} \exp(-2399/T)$	280-360		
$k_2 = 2.5 \times 10^{-15}$	298		
$(2.4 \pm 0.7) \times 10^{-13}$	295	Wallington and Hurley, 1992	RR (b)
$(2.4 \pm 0.5) \times 10^{-13}$	298	Tuazon et al., 1992	RR (b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC and the measured rate coefficient ratios were placed on an absolute basis by use of a rate coefficient of $k(Cl + C_2H_6) = 8.3 \times 10^{-11} \exp(-100/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k_1 = 2.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 6.3 \times 10^{-12} \exp(-965/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280-360 K.
$k_2 = 2.3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 7.0 \times 10^{-12} \exp(-2400/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280-360 K.

Reliability

$\Delta \log k_1 = \pm 0.15$ at 298 K.
$\Delta \log k_2 = \pm 0.5$ at 298 K.
$\Delta (E_1/R) = \Delta (E_2/R) = \pm 500$ K.

Comments on Preferred Values

The recommended value of the overall rate constant at room temperature is an average of all three relative rate studies, which show good agreement. The temperature dependence of k, k_1 and k_2 are taken from work of Yano and Tschuikow-Roux, (1986), which supersedes their previous data (Tschuikow-Roux et al., 1985).

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Yano, T. and Tschuikow-Roux, E.: J. Photochem., 32, 25, 1986.

IV.A2.100

$Cl + CH_2FCH_2F \rightarrow HCl + CHFCH_2F$

ΔH° = -4.6 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
2.8×10^{-11} exp[-(1065)/T]	280-360	Yano and Tschuikow-Roux, 1986	RR (a)
7.8×10^{-13}	298		
$(6.60 \pm 0.16) \times 10^{-13}$	298	Wallington et al., 1994	RR (b)
$(6.53 \pm 0.34) \times 10^{-13}$	298		RR (c)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC and the measured rate coefficient ratios were placed on an absolute basis by use of a rate coefficient of $k(Cl + C_2H_6) = 8.1 \times 10^{-11}$ exp(-100/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) Cl atoms were generated by the photolysis of Cl_2 in presence of CH_2FCH_2F-CH_4 in air at 930 mbar total pressure. Loss of reactants was monitored by FTIR. The measured rate coefficient ratio $k(Cl + CH_2FCH_2F)/k(Cl + CH_4) = (6.60 \pm 0.16)$ was placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) Cl atoms were generated by the photolysis of Cl_2 in presence of CH_2FCH_2F-CH_3Cl mixtures in air at 930 mbar total pressure. Loss of reactants was monitored by FTIR. The measured rate coefficient ratio $k(Cl + CH_2FCH_2F)/k(Cl + CH_3Cl) = (1.36 \pm 0.07)$ was placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_3Cl) = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 7.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.5 \times 10^{-11}$ exp(-1065/T) cm^3 molecule^{-1} s^{-1} over the temperature range 280-360 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

The recommended value at 298 K is an average of the rate constants obtained by the relative rate studies of Yano and Tschuikow-Roux (1986) and Wallington et al. (1994). The expression for the temperature dependence is taken from Yano and Tschuikow-Roux (1986), modified to reproduce the recommended value at 298 K.

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Yano, T. and Tschuikow-Roux, E.: J. Photochem., 32, 25, 1986.

IV.A2.101

$Cl + CH_3CF_3 \rightarrow HCl + CH_2CF_3$

$\Delta H^\circ = 18.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$< 1 \times 10^{-14}$	298	Hitsuda et al., 2001	PLP-LIF (a)
Relative Rate Coefficients			
6.9×10^{-12} exp(-3720/T)	281-368	Tschuikow-Roux et al., 1985	RR (b)
2.6×10^{-17}	298		

Comments

(a) Laser photolysis of HCl at 193 nm as Cl atom source. Both Cl($^2P_{3/2}$) and Cl($^2P_{1/2}$) detected by VUV-LIF.

(b) Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC and the measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(Cl + CH_4) = 6.6×10^{-12} exp(-1240/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 2.6 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.9 \times 10^{-12}$ exp(-3720/T) cm^3 molecule^{-1} s^{-1} over the temperature range 280-370 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The recommended value is based on the results of the relative rate study of Tschuikow-Roux et al., (1985). The room temperature upper limit to k of Hitsuda et al. (2001) is consistent with this.

References

Hitsuda, K., Takahashi, K., Matsumi, Y. and Wallington, T. J.: J. Phys. Chem. A, 105, 5131, 2001.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Tschuikow-Roux, E., Yano, T. and Niedzielski, J.: J. Chem. Phys., 82, 65, 1985.

IV.A2.102

$$\mathbf{Cl + CH_2FCHF_2 \rightarrow HCl + CH_2FCF_2 \quad (1)}$$
$$\mathbf{\rightarrow HCl + CHFCHF_2 \quad (2)}$$

$\Delta H°(1)$ = 2.2 kJ·mol^{-1}
$\Delta H°(2)$ = 0.0 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$k_1 = 3.3 \times 10^{-12}$ exp(-1450/T)	281-368	Tschuikow-Roux et al., 1985	RR (a)
$k_1 = 2.5 \times 10^{-14}$	298		
$k_2 = 4.6 \times 10^{-12}$ exp(-1560/T)	281-368		
$k_2 = 2.5 \times 10^{-14}$	298		

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC and the measured rate coefficient ratios were placed on an absolute basis by use of a rate coefficient of k(Cl + CH_4) = 6.6 × 10^{-12} exp(-1240/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k_1 = 2.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 3.3 \times 10^{-12}$ exp(-1450/T) cm^3 molecule^{-1} s^{-1} over the temperature range 280-370 K.
$k_2 = 2.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 4.6 \times 10^{-12}$ exp(-1560/T) cm^3 molecule^{-1} s^{-1} over the temperature range 280-370 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.5$ at 298 K.
$\Delta (E/R)_1 = \Delta (E/R)_2 = \pm 500$ K.

Comments on Preferred Values

The recommended values are based on the results of the single determination of this rate constant by Tschuikow-Roux et al. (1985).

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Tschuikow-Roux, E., Yano, T. and Niedzielski, J.: J. Chem. Phys., 82, 65, 1985.

IV.A2.103

$Cl + CH_3CF_2Cl \rightarrow HCl + CH_2CF_2Cl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.6 \pm 2.0) \times 10^{-16}$	297	Sawerysyn et al., 1992	DF-MS
$<4.4 \times 10^{-15}$	298	Warren and Ravishankara, 1993	PLP-RF
$1.5 \times 10^{-12} \exp[-(2420 \pm 400)/T]$	296-438	Talhaoui et al., 1996	DF-MS
$(4.7 \pm 1.3) \times 10^{-16}$	296		
Relative Rate Coefficients			
$(3.90 \pm 0.52) \times 10^{-16}$	295	Wallington and Hurley, 1992	RR (a)
$(3.7 \pm 0.8) \times 10^{-16}$	298	Tuazon et al., 1992	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 4.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.4 \times 10^{-12} \exp(-2420/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 296-440 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred value of the rate constant at 298 K is based on the results reported by Wallington and Hurley (1992), Tuazon et al. (1992) and Talhaoui et al. (1996). The latter study supersedes the work of Sawerysyn et al. (1992). The single temperature dependent study of Talhaoui et al. (1996) forms the basis for the recommendation of k(T), with the A-factor adjusted to reproduce the recommended value of k at 298 K.

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Sawerysyn, J. P., Talhaoui, A., Meriaux, B. and Devolder, P.: Chem. Phys. Lett., 198, 197, 1992.
Talhaoui, A., Devolder, L. P., Meriaux, B., Sawerysyn, J.-P., Rayez, M.-T. and Rayez, J.-C.: J. Phys. Chem., 100, 13531, 1996.
Tuazon, E. C., Atkinson, R. and Corchnoy, S. B.: Int. J. Chem. Kinet., 24, 639, 1992.
Wallington, T. J. and Hurley, M. D.: Chem. Phys. Lett., 189, 437, 1992.
Warren, R. F. and Ravishankara, A. R.: Int. J. Chem. Kinet., 25, 833, 1993.

IV.A2.104

$Cl + CH_3CFCl_2 \rightarrow HCl + CH_2CFCl_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.2) \times 10^{-15}$	297	Sawerysyn et al., 1992	DF-MS
$1.0 \times 10^{-12}\exp[-(1800 \pm 500)/T]$	298-376	Warren and Ravishankara, 1993	PLP-RF
$(2.4 \pm 0.4)\times 10^{-15}$	298		
$3.0 \times 10^{-12} \exp[-(2220 \pm 150)/T]$	299-429	Talhaoui et al., 1996	DF-MS
$(1.7 \pm 0.2) \times 10^{-15}$	299		
Relative Rate Coefficients			
$(2.0 \pm 0.2) \times 10^{-15}$	295	Wallington and Hurley, 1992	RR (a)
$(2.4 \pm 0.5) \times 10^{-15}$	298	Tuazon et al., 1992	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio was placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 2.1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.7 \times 10^{-12} \exp(-2000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290-380 K.

Reliability

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

Comments on Preferred Values

The preferred value at 298 K is an average of the results reported by Wallington and Hurley (1992), Tuazon et al. (1992), Warren and Ravishankara (1993) and Talhaoui et al. (1996). The expression for the temperature dependence is an average of the values of E/R obtained by Warren and Ravishankara (1992) and Talhaoui et al. (1996). The data in Sawerysyn et al. (1992) are superseded by those in Talhaoui et al. (1996).

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Sawerysyn, J. P., Talhaoui, A., Meriaux, B. and Devolder, P.: Chem. Phys. Lett., 198, 197, 1992.
Talhaoui, A., Devolder, L. P., Meriaux, B., Sawerysyn, J.-P., Rayez, M.-T. and Rayez, J.-C.: J. Phys. Chem., 100, 13531, 1996.
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Wallington, T.J. and Hurley, M. D.: Chem. Phys. Lett., 189, 437, 1992.
Warren, R. F. and Ravishankara, A. R.: Int. J. Chem. Kinet., 25, 833, 1993.

IV.A2.105

$Cl + CH_3CCl_3 \rightarrow HCl + CH_2CCl_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$< 2.40 \times 10^{-14}$	259	Wine et al., 1982	PLP-RF
$< 3.68 \times 10^{-14}$	298		
$< 7.74 \times 10^{-14}$	356		
$2.8 \times 10^{-12} \exp[-(1790 \pm 320)/T]$	298-418	Talhaoui et al., 1996	DF-MS
$(7.1 \pm 1.1) \times 10^{-15}$	298		
Relative Rate Coefficients			
$(9.9 \pm 2.0) \times 10^{-15}$	296	Platz et al., 1995	RR (a)

Comments

(a) Photolysis of Cl_2-CH_3CCl_3-CD_4 mixtures in air or N_2 at 930 mbar total pressure, with the loss of reactants monitored by FTIR. A value of $k(Cl + CH_3CCl_3)/k(Cl + CD_4) = (1.62 \pm 0.05)$ was obtained and placed on an absolute basis using $k(Cl + CD_4) = 6.1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (Wallington and Hurley, 1992).

Preferred Values

$k = 7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.8 \times 10^{-12} \exp(-1790/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290-420 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred values of k are based on the direct study of Talhaoui et al. (1996), which is consistent with the upper limits of Wine et al. (1982) and with the room temperature relative rate study of Platz et al. (1995).

References

Platz, J., Nielsen, O. J., Sehested, J. and Wallington, T. J.: J. Phys. Chem., 99, 6570, 1995.
Talhaoui, A., Devolder, L. P., Meriaux, B., Sawerysyn, J.-P., Rayez, M.-T. and Rayez, J.-C.: J. Phys. Chem., 100, 13531, 1996.
Wallington, T. J. and Hurley, M. D.: Chem. Phys. Lett., 189, 437, 1992.
Wine, P. H., Semmes, D. H. and Ravishankara, A. R.: Chem. Phys. Lett., 90, 128, 1982.

IV.A2.106

$$\mathbf{Cl + CH_2FCF_3 \rightarrow HCl + CHFCF_3}$$

$\Delta H^\circ = 1.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.6 \pm 0.3) \times 10^{-15}$	297	Sawerysyn et al., 1992	DF-MS
$3.2 \times 10^{-12} \exp[-(2300 \pm 70)/T]$	298-423	Louis et al., 1997	DF-MS
$(1.4 \pm 0.3) \times 10^{-15}$	298		
Relative Rate Coefficients			
$(1.38 \pm 0.18) \times 10^{-15}$	295	Wallington and Hurley, 1992	RR (a)
$(1.6 \pm 0.3) \times 10^{-15}$	298	Tuazon et al., 1992	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio was placed on an absolute basis by use of a rate coefficient of k(Cl + CH_4) = 1.0×10^{-13} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.4 \times 10^{-12} \exp(-2300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 298-430 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported by Louis et al. (1997), Wallington and Hurley (1992) and Tuazon et al. (1992) which are in good agreement. The room temperature rate constant of Sawerysyn et al. (1992) is considered to be superseded by that measured in the same group by Louis et al. (1997). The temperature dependence of k is taken from Louis et al. (1997) with the A-factor adjusted to reproduce the recommended value of k at 298 K.

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Louis, J., Talhaoui, A., Sawerysyn, J. P., Rayez, M.-T. and Rayez, J.-C.: J. Phys. Chem. A,. 101, 8503, 1997.
Sawerysyn, J. P., Talhaoui, A., Meriaux, B. and Devolder, P.: Chem. Phys. Lett., 198, 197, 1992.
Tuazon, E. C., Atkinson, R. and Corchnoy, S. B.: Int. J. Chem. Kinet., 24, 639, 1992.
Wallington, T. J. and Hurley, M. D.: Chem. Phys. Lett., 189, 437, 1992.

IV.A2.107

$Cl + CHF_2CHF_2 \rightarrow HCl + CF_2CHF_2$

$\Delta H^\circ = 6.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
8.9×10^{-12} exp(-2444/T)	280-360	Yano and Tschuikow-Roux, 1986	RR (a)
2.4×10^{-15}	298		
1.9×10^{-15}	298	Nielsen et al., 1992	RR (b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC. The measured rate coefficient ratio was placed on an absolute basis by use of $k(Cl + C_2H_6) = 8.3 \times 10^{-11}$ exp(-100/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio was placed on an absolute basis by use of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 2.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.9 \times 10^{-12}$ exp(-2440/T) cm^3 molecule^{-1} s^{-1} over the temperature range 280-360 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The recommended value at 298 K is an average of the results of Nielsen et al. (1992) and Yano and Tschuikow-Roux (1986). The expression for the temperature dependence is that of Yano and Tschuikow-Roux (1986), with the A-factor modified to reproduce the recommended value of k at 298 K.

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Nielsen, O. J., Ellermann, T., Sehested, J. and Wallington, T. J.: J. Phys. Chem., 96, 10875, 1992.
Yano, T. and Tschuikow-Roux, E.: J. Photochem., 32, 25, 1986.

IV.A2.108

$$\mathbf{Cl + CHF_2CF_3 \rightarrow HCl + CF_2CF_3}$$

$\Delta H^\circ = 10.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.4 \pm 0.5) \times 10^{-16}$	298	Tuazon et al., 1992	RR (a)
$(2.6 \pm 0.6) \times 10^{-16}$	295	Sehested et al., 1993	RR (b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient was placed on an absolute basis by use of a rate coefficient of k(Cl + CH_4) = 1.0×10^{-13} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient was ratio placed on an absolute basis by use of a rate coefficient of k(Cl + CH_3CF_2Cl) = 4.1×10^{-16} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 2.5 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value at 298 K is based on the results of the relative rate studies of Tuazon et al. (1992) and Sehested et al. (1993), which are in good agreement. Since studies have only been carried out at room temperature, no temperature dependence is recommended.

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Sehested, J., Ellermann, T., Nielsen, O. J., Wallington, T. J. and Hurley, M. D.: Int. J. Chem. Kinet., 25, 701, 1993.
Tuazon, E. C., Atkinson, R. and Corchnoy, S. B.: Int. J. Chem. Kinet., 24, 639, 1992.

IV.A2.109

$Cl + CHFClCF_3 \rightarrow HCl + CFClCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.16 \times 10^{-12} \exp[-(1800 \pm 150)/T]$	276-376	Warren and Ravishankara, 1993	PLP-RF
$(2.62 \pm 0.50) \times 10^{-15}$	298		
Relative Rate Coefficients			
$(2.7 \pm 0.6) \times 10^{-15}$	298	Tuazon et al. 1992	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio was placed on an absolute basis by use of a rate coefficient of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 2.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.1 \times 10^{-12} \exp(-1800/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270-380 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported by Warren and Ravishankara (1993) and Tuazon et al. (1992), which are in good agreement. The recommended temperature dependence is that reported by Warren and Ravishankara (1993), the only study carried out over a range of temperatures.

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Tuazon, E. C., Atkinson, R. and Corchnoy, S. B.: Int. J. Chem. Kinet., 24, 639, 1992.
Warren, R. F. and Ravishankara, A. R.: Int. J. Chem. Kinet., 25, 833, 1993.

IV.A2.110

$$\mathbf{Cl + CHCl_2CF_3 \rightarrow HCl + CCl_2CF_3}$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
3.94×10^{-12} exp[-(1740 ± 100)/T]	276-382	Warren and Ravishankara, 1993	PLP-RF
(1.15 ± 0.30) × 10^{-14}	298		
Relative Rate Coefficients			
(1.22 ± 0.18) × 10^{-14}	295	Wallington and Hurley, 1992	RR (a)
(1.4 ± 0.3) × 10^{-14}	298	Tuazon et al. 1992	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio was placed on an absolute basis by use of a rate coefficient of k(Cl + CH_4) = 1.0×10^{-13} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.4 \times 10^{-12}$ exp(-1740/T) cm^3 molecule^{-1} s^{-1} over the temperature range 270-380 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported by Warren and Ravishankara (1993), Wallington and Hurley (1992), and Tuazon et al. (1992), which are in good agreement. The recommended temperature dependence is that reported by Warren and Ravishankara, (1993) the only study carried out over a range of temperatures.

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Tuazon, E. C., Atkinson, R. and Corchnoy, S. B.: Int. J. Chem. Kinet., 24, 639, 1992.
Wallington, T. J. and Hurley, M. D.: Chem. Phys. Lett., 189, 437, 1992.
Warren, R. F. and Ravishankara, A. R.: Int. J. Chem. Kinet., 25, 833, 1993.

IV.A2.111

$HO + CH_3Cl \rightarrow H_2O + CH_2Cl$

$\Delta H° = -79.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.6 \pm 0.8) \times 10^{-14}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$4.1 \times 10^{-12} \exp[-(1359 \pm 151)/T]$	298-423	Perry et al., 1976	FP-RF
$(4.4 \pm 0.5) \times 10^{-14}$	298		
$1.84 \times 10^{-12} \exp[-(1098 \pm 36)/T]$	250-350	Davis et al., 1976	FP-RF
$(4.29 \pm 0.21) \times 10^{-14}$	298		
$(4.10 \pm 0.69) \times 10^{-14}$	297	Paraskevopoulos et al., 1981	FP-RA
$2.21 \times 10^{-21} T^{3.08} \exp[-(232 \pm 423)/T]$	247-483	Jeong and Kaufman, 1982;	DF-RF
$(3.95 \pm 0.26) \times 10^{-14}$	293	Jeong et al., 1984	
$(5.3 \pm 0.8) \times 10^{-14}$	298	Brown et al., 1990	DF-RF
$2.90 \times 10^{-14} T^{0.89} \exp[-(1447 \pm 75)/T]$	295-955	Taylor et al., 1993	PLP-LIF (a)
$(4.9 \pm 0.6) \times 10^{-14}$	295		
$1.24 \times 10^{-13} T^{0.5} \exp[-(1210 \pm 52)/T]$	224-398	Herndon et al., 2001	PLP-LIF
$(3.32 \pm 0.10) \times 10^{-14}$	298		
Relative Rate Coefficients			
7.8×10^{-14}	298	Cox et al., 1976	RR (b)
$5.35 \times 10^{-18} T^2 \exp[-(775 \pm 74)/T]$	293-358	Hsu and DeMore, 1994	RR (c)
3.53×10^{-14}	298		

Comments

(a) These data supersede the earlier data from this group (Taylor et al., 1989).

(b) HO radicals were generated by the photolysis of HONO-air mixtures at one atmosphere total pressure. Relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based on the effect of CH_3Cl on NO formation and a rate coefficient for the reaction of HO radicals with CH_4 of 6.4×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation), the rate coefficient cited in the table is obtained.

(c) HO radicals were generated by the UV photolysis of O_3 in the presence of water vapor. The concentrations of CH_3Cl and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3Cl)/k(HO + CH_3CHF_2) = (1.91 \pm 0.45) \exp[-(195 \pm 74)/T]$ is placed on an absolute base by using a rate coefficient of $k(HO + CH_3CHF_2) = 2.80 \times 10^{-18} T^2 \exp(-580/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 3.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.1 \times 10^{-12} \exp(-1210/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-300 K.

Reliability

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

Comments on Preferred Values

At room temperature, the absolute rate coefficients of Herndon et al. (2001) are significantly lower than those from the earlier studies of Perry et al (1976), Davis et al. (1976), Cox et al. (1976), Paraskevopoulos et al. (1981), Jeong and Kaufman (1982), Brown et al. (1990) and Taylor et al. (1993), but are in good agreement with the absolute rate coefficient of Howard and Evenson (1976) and the relative rate coefficients of Hsu and DeMore (1994). Furthermore, the relative rate coefficients of Hsu and DeMore (1994) are in excellent agreement with the absolute rate coefficients of Herndon et al. (2001) over the temperature range common to both studies (293–358 K), and at 363 and 401 K the rate coefficients of Jeong and Kaufman (1982) are in good agreement with the data of Herndon et al. (2001). The absolute rate coefficients of Herndon et al. (2001) have been fitted to the three parameter equation $k = CT^2$ exp(-D/T), resulting in k = 4.34 × 10^{-18} T^2 exp(-700/T) cm^3 $\mathrm{molecule}^{-1}$ s^{-1} over the temperature range 224–398 K. The preferred Arrhenius expression, $k = A$ exp(-B/T), is centered on a mid-range temperature, T_m, of 255 K and is obtained from the three parameter equation with $A = C\ e^2\ T_m^2$ and $B = D + 2T_m$. As noted above, the rate coefficients obtained from the relative rate study of Hsu and DeMore (1994) are in excellent agreement with the preferred values.

Gola et al. (2005) have measured a rate coefficient ratio of $k(\mathrm{HO} + {}^{12}\mathrm{CH_3Cl})/k(\mathrm{HO} + {}^{13}\mathrm{CH_3Cl})$ = 1.059 ± 0.008 at 298 ± 2 K, and the deuterium isotope effect for the reaction of HO radicals with $\mathrm{CD_3Cl}$, of $k(\mathrm{HO} + \mathrm{CH_3Cl})/k(\mathrm{HO} + \mathrm{CD_3Cl})$ = 3.9 ± 0.4 at 298 ± 2 K.

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IV.A2.112

$HO + CH_2FCl \rightarrow H_2O + CHFCl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.7 \pm 0.6) \times 10^{-14}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
2.84×10^{-12} exp[-$(1259 \pm 50)/T$]	245-375	Watson et al., 1977	FP-RF
$(4.21 \pm 0.41) \times 10^{-14}$	298		
3.1×10^{-12} exp[-$(1320 \pm 100)/T$]	273-373	Handwerk and Zellner, 1978	FP-RA
$(3.5 \pm 0.7) \times 10^{-14}$	293		
$(4.45 \pm 0.67) \times 10^{-14}$	297	Paraskevopoulos et al., 1981	FP-RA
1.57×10^{-19} $T^{2.41}$ exp[-$(307 \pm 382)/T$]	250-486	Jeong and Kaufman, 1982;	DF-RF
$(4.94 \pm 0.30) \times 10^{-14}$	295	Jeong et al., 1984	
Relative Rate Coefficients			
1.46×10^{-12} exp[-$(1076 \pm 24)/T$]	293-371	DeMore, 1996	RR (a)
3.95×10^{-14}	298		

Comments

(a) HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of H_2O, and CH_2Cl_2 was used as the reference compound. CH_2FCl and CH_2Cl_2 were monitored by FTIR spectroscopy, and a rate coefficient ratio of k(HO + CH_2FCl)/k(HO + CH_2Cl_2) = 0.81 exp[-$(216 \pm 24)/T$] was determined. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(HO + CH_2Cl_2) = 1.8×10^{-12} exp(-860/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 3.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.6 \times 10^{-12}$ exp(-1105/T) cm^3 molecule^{-1} s^{-1} over the temperature range 240-300 K.

Reliability

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

Comments on Preferred Values

The absolute rate coefficients of Jeong and Kaufman (1982) are significantly higher than the absolute and relative rate data of Howard and Evenson (1976), Watson et al. (1977), Handwerk and Zellner, 1978), Paraskevopoulos et al. (1981) and DeMore (1996), with the discrepancies being more marked at the lowest temperatures studied by Jeong and Kaufman (250 and 295 K). The rate coefficients measured by Howard and Evenson (1976), Watson et al. (1977), Handwerk and Zellner (1978), Paraskevopoulos et al. (1981) and DeMore (1996) are in reasonably good agreement, and the rate coefficients from these studies have been fitted to the three parameter expression $k = CT^2$ exp($-D/T$), resulting in $k = 3.03 \times 10^{-18}$ T^2 exp(-574/T) cm^3 molecule^{-1} s^{-1} over the temperature range 245–375 K. The preferred Arrhenius expression, $k = A$ exp($-B/T$), is centered on a mid-range temperature, T_m, of 265 K and is obtained from the three parameter equation with $A = Ce^2\ T_m^2$ and $B = D + 2T_m$.

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IV.A2.113

$HO + CH_2Cl_2 \rightarrow H_2O + CHCl_2$

ΔH° = -94.6 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.55 \pm 0.34) \times 10^{-13}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$(1.45 \pm 0.20) \times 10^{-13}$	298.5	Perry et al., 1976	FP-RF
$4.27 \times 10^{-12} \exp[-(1094 \pm 82)/T]$	245-375	Davis et al., 1976	FP-RF
$(1.16 \pm 0.05) \times 10^{-13}$	298		
$1.61 \times 10^{-19}\ T^{2.54} \exp[-(186 \pm 493)/T]$	251-455	Jeong and Kaufman, 1982;	DF-RF
$(1.53 \pm 0.095) \times 10^{-13}$	292	Jeong et al., 1984	
$4.01 \times 10^{-15}\ T^{1.09} \exp[-(771 \pm 48)/T]$	295-955	Taylor et al., 1993	PLP-LIF (a)
$(1.47 \pm 0.18) \times 10^{-13}$	295		
$2.61 \times 10^{-12} \exp[-(944 \pm 29)/T]$	277-370	Villenave et al., 1997	FP-RF
$(1.10 \pm 0.05) \times 10^{-13}$	298		
$6.6 \times 10^{-13}\ T^{0.5} \exp[-(721 \pm 32)/T]$	219-394	Herndon et al., 2001	PLP-LIF
$(1.00 \pm 0.14) \times 10^{-13}$	298		
Relative Rate Coefficients			
9.5×10^{-14}	298	Cox et al., 1976	RR (b)
$2.72 \times 10^{-18}\ T^2 \exp[-(286 \pm 29)/T]$	293-360	Hsu and DeMore, 1994	RR (c,d)
9.25×10^{-14}	298		
$1.96 \times 10^{-18}\ T^2 \exp[-(104 \pm 20)/T]$	298-368	Hsu and DeMore, 1994	RR (c,e)
1.22×10^{-13}	298		

Comments

(a) These data supersede the earlier data from this group (Taylor et al., 1989).

(b) HO radicals were generated by the photolysis of HONO-air mixtures at 1.013 bar pressure. Relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based on the effect of CH_2Cl_2 on NO formation and a rate coefficient for the reaction of HO radicals with CH_4 of 6.4×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation), the rate coefficient cited in the table is obtained.

(c) HO radicals were generated by the UV photolysis of O_3 in the presence of water vapor. CH_2Cl_2 and CH_3CHF_2 (or CH_3CH_2F) concentrations were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(HO + CH_2Cl_2)/k(HO + CH_3CHF_2) = (0.97 \pm 0.09) \exp[(294 \pm 29)/T]$ and $k(HO + CH_2Cl_2)/k(HO + CH_3CH_2F) = (0.32 \pm 0.02) \exp[(171 \pm 20)/T]$ are placed on an absolute basis by using rate coefficients of $k(HO + CH_3CHF_2) = 2.80 \times 10^{-18}\ T^2 \exp(-580/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation) and $k(HO + CH_3CH_2F) = 6.12 \times 10^{-18}\ T^2 \exp(-275/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(d) Relative to $HO + CH_3CHF_2$.

(e) Relative to $HO + CH_3CH_2F$.

Preferred Values

$k = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.8 \times 10^{-12} \exp(-860/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210-400 K.

Reliability

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

Comments on Preferred Values

The absolute room temperature rate coefficients of Howard and Evenson (1976), Perry et al. (1976), Jeong and Kaufman (1982) and Taylor et al. (1993) are significantly higher than those of Davis et al. (1976), Villenave et al. (1997) and Herndon et al. (2001), possibly because of the presence of reactive impurities (including stabilizers) present in the CH_2Cl_2 samples used (Villenave et al., 1997; Herndon et al., 2001). The relative rate data of Cox et al. (1976) and Hsu and DeMore (1994) are in reasonable agreement with the absolute rate coefficients of Villenave et al. (1997) and Herndon et al. (2001). An Arrhenius plot of the absolute rate data of Villenave et al. (1997) and Herndon et al. (2001) shows little or no evidence for curvature over the temperature range studied (219–394 K). Accordingly, the preferred Arrhenius expression is obtained from a unit-weighted least-squares analysis of the absolute rate coefficients of Villenave et al. (1997) and Herndon et al. (2001). The room temperature relative rate constant of Cox et al. (1976) agrees well with the preferred 298 K value, while the rate coefficients of Hsu and DeMore (1994) relative to HO + CH_3CHF_2 are ∼5-10% lower than the preferred values and those relative to HO + CH_3CH_2F are ∼15-20% higher than the preferred values over the temperature ranges 298–360 K and 298–368 K, respectively.

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IV.A2.114

$$\mathbf{HO + CHF_2Cl \rightarrow H_2O + CF_2Cl}$$

ΔH° = -74.4 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.21×10^{-12} exp[-(1636 ± 151)/T]	297-434	Atkinson et al., 1976	FP-RF
$(4.75 \pm 0.48) \times 10^{-15}$	296.9		
$(3.4 \pm 0.7) \times 10^{-15}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
9.25×10^{-13} exp[-(1575 ± 71)/T]	250-350	Watson et al., 1977	FP-RF
$(4.8 \pm 0.46) \times 10^{-15}$	298		
1.20×10^{-12} exp[-(1657 ± 39)/T]	253-427	Chang and Kaufman, 1977	DF-RF
$(4.25 \pm 0.28) \times 10^{-15}$	296		
2.1×10^{-12} exp[-(1780 ± 150)/T]	263-373	Handwerk and Zellner, 1978	FP-RA
$(4.6 \pm 0.8) \times 10^{-15}$	293		
9.5×10^{-12} exp[-(2300 ± 200)/T]	294-426	Clyne and Holt, 1979	DF-RF
$(3.3 \pm 0.7) \times 10^{-15}$	294		
$(4.58 \pm 0.59) \times 10^{-15}$	297	Paraskevopoulos et al., 1981	FP-RA
5.03×10^{-28} $T^{5.11}$ exp[-(252 ± 780)/T]	293-492	Jeong and Kaufman, 1982;	DF-RF
$(4.83 \pm 0.32) \times 10^{-15}$	293	Jeong et al., 1984	
8.1×10^{-13} exp[-(1516 ± 53)/T]	298-460	Orkin and Khamaganov, 1993	DF-EPR
$(4.9 \pm 0.45) \times 10^{-15}$	298		
1.74×10^{-12} exp[-(1701 ± 39)/T]	302-382	Yujing et al., 1993	DF-RF
5.99×10^{-15}	302		
Absolute Rate Coefficients			
1.31×10^{-22} $T^{3.28}$ exp[-(361 ± 564)/T]	294-807	Fang et al., 1996	PLP-LIF
$(4.65 \pm 0.66) \times 10^{-15}$	294		
Relative Rate Coefficients			
4.44×10^{-21} $T^{2.82}$ exp[-(645 ± 45)/T]	298-366	Hsu and DeMore, 1995	RR (a)
4.83×10^{-15}	298		

Comments

(a) HO radicals were generated by the UV photolysis of O_3 in the presence of water vapor. The concentrations of CHF_2Cl and CH_4 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CHF_2Cl)/k(HO + CH_4) = (0.24 \pm 0.03) \exp[(342 \pm 45)/T]$ is placed on an absolute basis by using a rate coefficient of $k(HO + CH_4) = 1.85 \times 10^{-20}\ T^{2.82} \exp(-987/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 4.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.9 \times 10^{-13} \exp(-1530/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240-300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta (E/R) = \pm 150$ K.

Comments on Preferred Values

The absolute rate coefficients of Atkinson et al. (1975), Howard and Evenson (1976), Watson et al. (1977), Chang and Kaufman (1977), Handwerk and Zellner (1978), Paraskevopoulos et al. (1981), Jeong and Kaufman (1982), Orkin and Khamaganov (1993) and Fang et al. (1996) are in good agreement, and the relative rate coefficients of Hsu and DeMore (1995) agree well with these absolute rate coefficients. The absolute rate coefficients of Clyne and Holt (1979) exhibit a significantly higher temperature dependence than those determined in the other absolute rate studies, and the rate coefficients of Yujing et al. (1993) are significantly higher those of Atkinson et al. (1975), Howard and Evenson (1976), Watson et al. (1977), Chang and Kaufman (1977), Handwerk and Zellner (1978), Paraskevopoulos et al. (1981), Jeong and Kaufman (1982), Orkin and Khamaganov (1993) and Fang et al. (1996). Accordingly, the studies of Clyne and Holt (1979) and Yujing et al. (1993) are not used in the evaluation of the rate coefficient for this reaction. The absolute rate coefficients of Atkinson et al. (1975), Howard and Evenson (1976), Watson et al. (1977), Chang and Kaufman (1977), Handwerk and Zellner (1978), Paraskevopoulos et al. (1981), Jeong and Kaufman (1982), Orkin and Khamaganov (1993) and Fang et al. (1996) have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.52 \times 10^{-18}\ T^2 \exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–807 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered on a mid-range temperature, T_m, of 265 K and is obtained from the three parameter equation with $A = Ce^2\ T_m^2$ and $B = D + 2T_m$. The relative rate data of Hsu and DeMore (1995) agree to within 3% with the preferred values.

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IV.A2.115

$HO + CHFCl_2 \rightarrow H_2O + CFCl_2$

ΔH° = -83.2 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.6 \pm 0.4) \times 10^{-14}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
1.75×10^{-12} exp[-(1253 ± 151)/T]	298-422	Perry et al., 1976	FP-RF
$(2.7 \pm 0.3) \times 10^{-14}$	298.4		
1.87×10^{-12} exp[-(1245 ± 26)/T]	245-375	Watson et al., 1977	FP-RF
$(2.88 \pm 0.24) \times 10^{-14}$	298		
1.16×10^{-12} exp[-(1073 ± 40)/T]	241-396	Chang and Kaufman, 1977	DF-RF
$(3.04 \pm 0.11) \times 10^{-14}$	296		
4.8×10^{-12} exp[-(1400 ± 100)/T]	293-413	Clyne and Holt, 1979	DF-RF
$(3.54 \pm 0.26) \times 10^{-14}$	293		
$(3.39 \pm 0.87) \times 10^{-14}$	297	Paraskevopoulos et al., 1981	FP-RA
1.97×10^{-18} $T^{1.94}$ exp[-(382 ± 413)/T]	250-483	Jeong and Kaufman, 1982	DF-RF
$(3.37 \pm 0.22) \times 10^{-14}$	295	Jeong et al., 1984	
1.53×10^{-15} $T^{1.11}$ exp[-(1078 ± 262)/T]	295-810	Fang et al., 1996	PLP-LIF
$(2.48 \pm 0.67) \times 10^{-14}$	295		

Preferred Values

$k = 2.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.04 \times 10^{-12}$ exp(-1065/T) cm^3 molecule^{-1} s^{-1} over the temperature range 240-300 K.

Reliability

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

Comments on Preferred Values

The absolute rate coefficients of Clyne and Holt (1979) are significantly higher than those of Howard and Evenson (1976), Perry et al. (1976), Watson et al. (1977), Chang and Kaufman (1977), Paraskevopoulos et al. (1981), Jeong and Kaufman (1982) and Fang et al. (1996), and are therefore not used in the evaluation. The absolute rate coefficients of Howard and Evenson (1976), Perry et al. (1976), Watson et al. (1977), Chang and Kaufman (1977), Paraskevopoulos et al. (1981), Jeong and Kaufman (1982) and Fang et al. (1996) have been fitted to the three parameter equation $k = CT^2$ exp(-D/T), resulting in $k = 2.00 \times 10^{-18}$ T^2 exp(-535/T) cm^3 molecule^{-1} s^{-1} over the temperature range 241–810 K. The preferred Arrhenius expression, $k = A$ exp(-B/T), is centered on a mid-range temperature, T_m, of 265 K and is obtained from the three parameter equation with $A = Ce^2\, T_m^2$ and $B = D + 2T_m$.

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IV.A2.116

$HO + CHCl_3 \rightarrow H_2O + CCl_3$

ΔH° = -104.6 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.01 \pm 0.15) \times 10^{-13}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
4.69×10^{-12} exp[-(1134 ± 108)/T]	245-375	Davis et al., 1976	FP-RF
$(1.14 \pm 0.07) \times 10^{-13}$	298		
6.91×10^{-20} $T^{2.65}$ exp[-(262 ± 398)/T]	249-487	Jeong and Kaufman, 1982;	DF-RF
$(1.01 \pm 0.065) \times 10^{-13}$	298	Jeong et al., 1984	
4.65×10^{-17} $T^{1.52}$ exp[-(261 ± 42)/T]	295-775	Taylor et al., 1993	PLP-LIF (a)
$(1.12 \pm 0.10) \times 10^{-13}$	295		
Relative Rate Coefficients			
1.53×10^{-13}	298	Cox et al., 1976	RR (b)
1.46×10^{-18} T^2 exp[-(85 ± 64)/T]	288-357	Hsu and DeMore, 1994	RR (c)
9.75×10^{-14}	298		

Comments

(a) These data supersede the earlier data from this group (Taylor et al., 1989).

(b) HO radicals were generated by the photolysis of HONO-air mixtures at 1.013 bar pressure. Relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based on the effect of $CHCl_3$ on NO formation and a rate coefficient for the reaction of HO radicals with CH_4 of 6.4×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation), the rate coefficient cited in the table is obtained.

(c) HO radicals were generated by the UV photolysis of O_3 in the presence of water vapor. The concentrations of $CHCl_3$ and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CHCl_3)/k(HO + CH_3CHF_2) = (0.52 \pm 0.11)$ exp[(495 ± 64)/T] is placed on an absolute base by using a rate coefficient of $k(HO + CH_3CHF_2) = 2.80 \times 10^{-18}$ T^2 exp(-580/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.05 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.8 \times 10^{-12}$ exp(-850/T) cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

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

Comments on Preferred Values

The measured rate data for this reaction exhibit a large amount of scatter, with the room temperature rate coefficients of Howard and Evenson (1976), Davis et al. (1976), Jeong and Kaufman (1982), Taylor et al. (1993) and Hsu and DeMore

(1994) ranging from 9.75 × 10^{-14} cm^3 $molecule^{-1}$ s^{-1} to 1.14 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. Furthermore, the temperature dependencies obtained by Davis et al. (1976), Jeong and Kaufman (1982), Taylor et al. (1993) and Hsu and DeMore (1994) differ significantly, with Davis et al. (1976) and Jeong and Kaufman (1982) determining larger temperature dependencies than obtained by Taylor et al. (1992) and Hsu and DeMore (1994). Note that only two rate coefficients have been measured at temperatures $<$288 K, one by Davis et al. (1976) at 245 K and the other by Jeong and Kaufman (1982) at 249 K.

The 298 K preferred value is an average of the room temperature rate coefficients of Howard and Evenson (1976), Davis et al. (1976), Jeong and Kaufman (1982), Taylor et al. (1993) and Hsu and DeMore (1994). The temperature dependence for the temperature range 240–300 K is obtained by averaging the Arrhenius activation energies centered on a mid-range temperature, T_m, of 265 K, with those of Jeong and Kaufman (1982), Taylor et al. (1993) and Hsu and DeMore (1994) being derived from the three parameter expressions cited in the table with $B = D + 2T_m$ (the Arrhenius activation energies being 1134 K for the Davis et al. (1976) study, 964 K for the Jeong and Kaufman (1982) study, 664 K for the Taylor et al. (1993) study and 615 K for the Hsu and DeMore (1994) study, all centered at 265 K). The preferred Arrhenius expression, which should not be used outside of the temperature range 240–300 K, leads to rate coefficients at 245 K and 249 K which are 28% and 8% higher than those measured by Davis et al. (1976) and Jeong and Kaufman et al. (1982), respectively (note that the recommended Arrhenius expression for the temperature range 240–300 K is equivalent to the three parameter equation $k = 3.47 \times 10^{-18}\ T^2$ exp(-320/T) cm^3 $molecule^{-1}$ s^{-1}). Clearly, additional studies of this reaction covering the temperature range ∼200–400 K are needed.

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IV.A2.117

$HO + CF_2Cl_2 \rightarrow HOCl + CF_2Cl$

$\Delta H^\circ = 99.0\ \mathrm{kJ \cdot mol^{-1}}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<1 \times 10^{-15}$	296-424	Atkinson et al., 1975	FP-RF
$<4 \times 10^{-16}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$<6 \times 10^{-16}$	478	Chang and Kaufman, 1977	DF-RF
$<1 \times 10^{-15}$	293	Clyne and Holt, 1979	DF-RF
Relative Rate Coefficients			
$<9 \times 10^{-17}$	298	Cox et al., 1976	RR (a)

Comments

(a) HO radicals were generated by the photolysis of HONO-air mixtures at 1.013 bar pressure. Relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based on the lack of effect of CF_2Cl_2 on NO formation and a rate coefficient for the reaction of HO radicals with CH_4 of 6.4×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation), the upper limit to the rate coefficient cited in the table is obtained.

Preferred Values

$k < 7 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k < 1 \times 10^{-12} \exp(-3540/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-480 K.

Comments on Preferred Values

The studies of Atkinson et al. (1975), Cox et al. (1976), Howard and Evenson (1976), Chang and Kaufman (1977) and Clyne and Holt (1979) all observed no reaction of HO radicals with CF_2Cl_2. The preferred upper limit Arrhenius expression is obtained from an assumed Arrhenius pre-exponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} and the upper limit rate coefficient at 478 K measured by Chang and Kaufman (1977). The resulting upper limit Arrhenius expression yields a 298 K upper limit rate coefficient which is consistent with the room temperature data of Atkinson et al. (1975), Cox et al. (1976), Howard and Evenson (1976) and Clyne and Holt (1979).

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IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.

IV.A2.118

$HO + CFCl_3 \rightarrow HOCl + CFCl_2$

$\Delta H^\circ = 80.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<1 \times 10^{-15}$	296-424	Atkinson et al., 1975	FP-RF
$<5 \times 10^{-16}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$<5 \times 10^{-16}$	480	Chang and Kaufman, 1977	DF-RF
$<1 \times 10^{-15}$	293	Clyne and Holt, 1979	DF-RF
Relative Rate Coefficients			
$<4 \times 10^{-17}$	298	Cox et al., 1976	RR (a)

Comments

(a) HO radicals were generated by the photolysis of HONO-air mixtures at 1013 mbar pressure. Relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based on the lack of effect of $CFCl_3$ on NO formation and a rate coefficient for the reaction of HO radicals with CH_4 of 6.4×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation), the upper limit to the rate coefficient cited in the table is obtained.

Preferred Values

$k < 5 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k < 1 \times 10^{-12} \exp(-3650/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-480 K.

Comments on Preferred Values

The studies of Atkinson et al. (1975), Cox et al. (1976), Howard and Evenson (1976), Chang and Kaufman (1977) and Clyne and Holt (1979) all observed no reaction of HO radicals with $CFCl_3$. The preferred upper limit Arrhenius expression is obtained from an assumed Arrhenius pre-exponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} and the upper limit at 480 K measured by Chang and Kaufman (1977). The resulting upper limit Arrhenius expression yields a 298 K upper limit rate coefficient which is consistent with the room temperature data of Atkinson et al. (1975), Cox et al. (1976), Howard and Evenson (1976) and Clyne and Holt (1979).

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IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.

IV.A2.119

$HO + CCl_4 \rightarrow HOCl + CCl_3$

ΔH° = 51.7 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<4 \times 10^{-15}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$<1 \times 10^{-15}$	293	Clyne and Holt, 1979	DF-RF
Relative Rate Coefficients			
$<9 \times 10^{-17}$	298	Cox et al., 1976	RR (a)

Comments

(a) HO radicals were generated by the photolysis of HONO-air mixtures at 1013 mbar pressure. Relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based on the lack of effect of CCl_4 on NO formation and a rate coefficient for the reaction of HO radicals with CH_4 of 6.4×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation), the upper limit to the rate coefficient cited in the table is obtained.

Preferred Values

$k < 5 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k < 1 \times 10^{-12} \exp(-2260/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range ∼250–300 K.

Comments on Preferred Values

The studies of Cox et al. (1976), Howard and Evenson (1976) and Clyne and Holt (1979) all observed no reaction of HO radicals with CCl_4. The preferred upper limit to the 298 K rate coefficient is based on the data of Cox et al. (1976), increased by a factor of 5 to take into account uncertainties in the number of NO molecules reacted per CCl_4 reacted, and the upper limit Arrhenius expression combines the preferred upper limit rate coefficient at 298 K with an assumed Arrhenius pre-exponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1}.

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IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.

IV.A2.120

HO + C_2HCl_3 → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.4) \times 10^{-12}$	296	Howard, 1976	DF-LMR
$5.32 \times 10^{-13} \exp[(445 \pm 41)/T]$	234-420	Chang and Kaufman, 1977	DF-RF
$(2.37 \pm 0.10) \times 10^{-12}$	296		
2.11×10^{-12}	305	Kirchner, 1983	DF-MS
$7.80 \times 10^{-13} \exp[(241 \pm 61)/T]$	300-459	Kirchner et al., 1990	DF-MS
$(1.76 \pm 0.17) \times 10^{-12}$	300		
$9.73 \times 10^{-13} \exp[(158.7 \pm 44.0)/T]$	291-650	Tichenor et al., 2000; 2001	PLP-LIF (a)
1.66×10^{-12}	298		
Relative Rate Coefficients			
$(4.3 \pm 1.3) \times 10^{-12}$	305 ± 2	Winer et al., 1976	RR (b)
$(2.64 \pm 0.37) \times 10^{-12}$	296	Edney et al., 1986	RR (c)
2.65×10^{-12}	300	Klöpffer et al., 1986	RR (d)

Comments

(a) This study was stated to supersede the earlier study of Jiang et al. (1993). Tichenor et al. (2000) fit their data, obtained over the temperature range 291–750 K, by the three parameter expression $k = 3.76 \times 10^{-21}\, T^{2.76} \exp[-(1266.3 \pm 41.2)/T]$ cm^3 molecule^{-1} s^{-1}.

(b) HO radicals were generated by the photolysis of NO_x-organic-air mixtures at ∼1 bar of air. Trichloroethene and 2-methylpropene (the reference compound) were monitored by GC. The measured rate coefficient ratio k(HO + trichloroethene)/k(HO + 2-methylpropene) = 0.088 (±30%) is placed on an absolute basis by use of a rate coefficient of k(HO + 2-methylpropene) = 4.94×10^{-11} cm^3 molecule^{-1} s^{-1} at 305 K (Atkinson, 1997).

(c) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at ∼1 bar of air. Trichloroethene and n-butane (the reference compound) were monitored by GC. The measured rate coefficient ratio k(HO + trichloroethene)/k(HO + n-butane) is placed on an absolute basis by use of a rate coefficient of k(HO + n-butane) = 2.33×10^{-12} cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 2003).

(d) HO radicals were generated by the photolysis of NO_x-organic-air mixtures at ∼1 bar of air. Trichloroethene and toluene (the reference compound) were monitored by GC. The measured rate coefficient ratio k(HO + trichloroethene)/k(HO + toluene) is placed on an absolute basis by use of a rate coefficient of k(HO + toluene) = 5.58×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K (Calvert et al., 2002).

Preferred Values

$k = 2.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.0 \times 10^{-13} \exp(565/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-300 K.

Reliability

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

Comments on Preferred Values

There is a significant degree of scatter in both the measured room temperature rate coefficients and the temperature dependence of the rate coefficient, with the room temperature relative rate coefficient from the Winer et al. (1976) study being much higher than those measured in the other studies (possibly because of the disparity between the reactivities of trichloroethene and the reference compound used). An Arrhenius plot of the rate coefficients of Howard (1976), Chang and Kaufman (1977) and Tichenor et al. (2001) suggests curvature [as also concluded by Tichenor et al. (2000)]. Accordingly, the absolute rate coefficients at $\leq$650 K from the studies of Howard (1976), Chang and Kaufman (1977) and Tichenor et al. (2001) were fitted to the three parameter expression $k = CT^2$ exp(-D/T), resulting in k = 6.06 × 10^{-19} T^2 exp(1084/T) cm^3 molecule^{-1} s^{-1} over the temperature range 234–650 K. The preferred Arrhenius expression, $k = A$ exp(-B/T), is centered on a mid-range temperature, T_m, of 260 K and is obtained from the three parameter equation with $A = C\ e^2\ T_m^2$ and $B = D + 2T_m$. The room temperature rate coefficients measured by Kirchner (1983), Edney et al. (1986), Klöpffer et al. (1986) and Kirchner et al. (1990), which are not used in the derivation of the preferred values, are in general agreement with the preferred values, and the temperature dependence reported by Kirchner et al. (1990) over the temperature range 300–459 K of B = -241 ± 61 K is in reasonable agreement with the value of B = -364 K derived from the preferred three parameter expression centered on a T_m of 360 K.

The reaction proceeds by initial HO radical addition to form the $HOCHClCCl_2$ and $HOCCl_2CHCl$ radicals, which under atmospheric conditions lead to the formation of Cl atoms, HC(O)Cl, $C(O)Cl_2$ and other, as yet unidentified, products (Tuazon et al., 1988; Kleindienst et al., 1989).

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IV.A2.121

HO + C_2Cl_4 → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.70 \pm 0.34) \times 10^{-13}$	296	Howard, 1976	DF-LMR
$9.44 \times 10^{-12} \exp[-(1199 \pm 55)/T]$	297-420	Chang and Kaufman, 1977	DF-RF
$(1.69 \pm 0.07) \times 10^{-13}$	297		
$5.53 \times 10^{-12} \exp[-(1034 \pm 13)/T]$	301-433	Kirchner, 1983;	DF-MS
$(1.73 \pm 0.17) \times 10^{-13}$	301	Kirchner et al., 1990	
$1.93 \times 10^{-22}\, T^{3.2} \exp[(660.8 \pm 54.6)/T]$	296.5-714	Tichenor et al., 2000	PLP-LIF (a)
$(1.45 \pm 0.16) \times 10^{-13}$	296.5		
$1.53 \times 10^{-12} \exp[-(688.2 \pm 67.5)/T]$	293-720	Tichenor et al., 2001	PLP-LIF
$(1.52 \pm 0.17) \times 10^{-13}$	293		
Relative Rate Coefficients			
$(2.2 \pm 0.7) \times 10^{-12}$	305 ± 2	Winer et al., 1976	RR (b)

Comments

(a) Tichenor et al. (2000) also fit their data to an Arrhenius expression, obtaining $k = 1.68 \times 10^{-12} \exp[-(764.2 \pm 79.1)/T]$ cm^3 molecule^{-1} s^{-1} over the same temperature range of 296.5–714 K.

(b) HO radicals were generated by the photolysis of NO_x-organic-air mixtures at ∼1 bar of air. Tetrachloroethene and 2-methylpropene (the reference compound) were monitored by GC. The measured rate coefficient ratio k(HO + tetrachloroethene)/k(HO + 2-methylpropene) = 0.044 (±30%) is placed on an absolute basis by use of a rate coefficient of k(HO + 2-methylpropene) = 4.94×10^{-11} cm^3 molecule^{-1} s^{-1} at 305 K (Atkinson, 1997).

Preferred Values

$k = 1.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.5 \times 10^{-12} \exp(-920/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290-420 K.

Reliability

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

Comments on Preferred Values

The room temperature absolute rate coefficients of Howard (1976), Chang and Kaufman (1977), Kirchner (1983), Kirchner et al. (1990) and Tichenor et al. (2000; 2001) are in good agreement. The relative rate coefficient of Winer et al. (1976) at 305 K is an order of magnitude higher, presumably in part because of the large difference in reactivities of tetrachloroethene and the 2-methylpropene reference compound. The preferred 298 K value is derived from the mean of the values of Howard (1976), Chang and Kaufman (1977), Kirchner et al. (1990), Tichenor et al. (2000) and Tichenor et al. (2001). The temperature dependence of the rate coefficient is the average of the Arrhenius activation energies reported by Chang and Kaufman, Kirchener et al. (1990), Tichenor et al. (2000) and Tichenor et al. (2001), with the pre-exponential factor being adjusted to fit the 298 K preferred value. No rate coefficients are available below 290 K, and additional studies involving measurements down to ≤ 220 K are clearly needed.

The reaction proceeds by initial HO radical addition to form the $HOCCl_2CCl_2$ radical, which under atmospheric conditions leads to the formation of Cl atoms, $C(O)Cl_2$ and other, as yet unidentified, products (Tuazon et al., 1988). The molar formation yield of $C(O)Cl_2$ was measured by Tuazon et al. (1988) to be $\sim$0.5 in both the presence and absence of a Cl atom scavenger.

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IV.A2.122

$HO + CH_3CF_2Cl \rightarrow H_2O + CH_2CF_2Cl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.83 \pm 0.42) \times 10^{-15}$	296	Howard and Evenson, 1976	DF-LMR
1.15×10^{-12} exp[-(1748 ± 30)/T]	273-375	Watson et al., 1977	FP-RF
$(3.22 \pm 0.48) \times 10^{-15}$	298		
1.8×10^{-12} exp[-(1790 ± 150)/T]	293-373	Handwerk and Zellner, 1978	FP-RA
$(3.7 \pm 0.7) \times 10^{-15}$	293		
3.3×10^{-12} exp[-(1800 ± 300)/T]	293-417	Clyne and Holt, 1979	DF-RF
$(6.7 \pm 1.3) \times 10^{-15}$	298		
$(4.63 \pm 1.73) \times 10^{-15}$	297	Paraskevopoulos et al., 1981	FP-RA
9.8×10^{-13} exp[-(1660 ± 200)/T]	270-400	Liu et al., 1990	FP-RF
$(4.02 \pm 1.0) \times 10^{-15}$	298		
2.6×10^{-13} exp[-(1230 ± 250)/T]	231-423	Brown et al., 1990	DF-RF
$(3.7 \pm 1.4) \times 10^{-15}$	303		
1.14×10^{-12} exp[-(1750 ± 75)/T]	223-374	Gierczak et al., 1991	DF-LMR/FP-LIF (a)
$(2.95 \pm 0.25) \times 10^{-15}$	298		
$(2.45 \pm 0.31) \times 10^{-15}$	270	Zhang et al., 1992	FP-RF
$(2.6 \pm 0.4) \times 10^{-15}$	293	Mörs et al., 1996	PLP-A
2.05×10^{-30} $T^{6.01}$ exp[(308 ± 522)/T]	295-808	Fang et al., 1997	PLP-LIF
$(3.77 \pm 0.43) \times 10^{-15}$	295		
Relative Rate Coefficients			
3.5×10^{-15}	298	Cox et al., 1976	RR (b)

Comments

(a) Experiments were carried out over the temperature range 223–427 K.

(b) HO radicals were generated by the photolysis of HONO-air mixtures at 1.013 bar pressure. Relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based on the effect of CH_3CF_2Cl on NO formation and a rate coefficient for the reaction of HO radicals with CH_4 of 6.4×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation), the rate coefficient cited in the table is obtained.

Preferred Values

$k = 3.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.5 \times 10^{-13}$ exp(-1685/T) cm^3 molecule^{-1} s^{-1} over the temperature range 220-300 K.

Reliability

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

Comments on Preferred Values

The rate coefficients obtained exhibit a large degree of scatter, especially at temperatures $\leq$305 K. In particular, the rate coefficients of Clyne and Holt (1979) and Brown et al. (1990) and, to a lesser extent, those of Handwerk and Zellner (1978), Paraskevopoulos et al. (1981), Liu et al. (1990), Zhang et al. (1992) and Fang et al. (1997) at room temperature and below are higher than those of Howard and Evenson (1976), Watson et al. (1977), Gierczak et al. (1991) and Mörs et al. (1996). Accordingly, the absolute rate coefficients of Howard and Evenson (1976), Watson et al. (1977), Gierczak et al. (1991) and Mörs et al. (1996) have been fitted to the three parameter equation $k = CT^2$ exp(-D/T), resulting in k = 1.77 $\times$ 10^{-18} T^2 exp(-1174/T) cm^3 molecule^{-1} s^{-1} over the temperature range 223–427 K. The preferred Arrhenius expression, $k = A$ exp(-B/T), is centered on a mid-range temperature, T_m, of 255 K and is obtained from the three parameter equation with $A = C\ e^2\ T_m^2$ and $B = D + 2T_m$.

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IV.A2.123

$HO + CH_3CFCl_2 \rightarrow H_2O + CH_2CFCl_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$3.6 \times 10^{-13} \exp[-(1140 \pm 210)/T]$	243-400	Liu et al., 1990	FP-RF
$(7.01 \pm 1.2) \times 10^{-15}$	298		
$5.8 \times 10^{-13} \exp[-(1100 \pm 250)/T]$	238-426	Brown et al., 1990	DF-RF
$(1.61 \pm 0.55) \times 10^{-14}$	297		
$1.47 \times 10^{-12} \exp[-(1640 \pm 100)/T]$	253-393	Talukdar et al., 1991	PLP-LIF/DF-LMR (a)
$(5.92 \pm 0.54) \times 10^{-15}$	298		
$(1.82 \pm 0.65) \times 10^{-15}$	250	Zhang et al., 1992	FP-RF (b)
$(2.01 \pm 0.90) \times 10^{-15}$	250		
$(3.39 \pm 0.82) \times 10^{-15}$	270		
$(4.80 \pm 1.46) \times 10^{-15}$	297		
$2.4 \times 10^{-12} \exp[-(1790 \pm 100)/T]$	298-479	Lancar et al., 1993	DF-EPR
$(5.7 \pm 1.5) \times 10^{-15}$	298		
$(4.6 \pm 0.8) \times 10^{-15}$	293	Mörs et al., 1996	FP-A
Relative Rate Coefficients			
$9.07 \times 10^{-21} T^{2.82} \exp[-(798 \pm 105)/T]$	298-358	Huder and DeMore, 1993	RR (c,d)
5.91×10^{-15}	298		
$1.78 \times 10^{-18} T^2 \exp[-(984 \pm 28)/T]$	298-358	Huder and DeMore, 1993	RR (c,e)
5.85×10^{-15}	298		

Comments

(a) Experiments were carried out down to 233 K, using highly purified samples. In the pulsed laser photolysis experiments, photolysis of HONO was used as the HO radical source to avoid photolysis of CH_3CFCl_2. An Arrhenius plot of the entire dataset showed curvature at the two lowest temperatures studied (233 and 249 K), and the cited Arrhenius expression was derived using only the rate coefficients measured at $\geq$253 K.

(b) HO radicals were generated by the pulsed photolysis of H_2O. Experiments carried out with reduced flash energies or water vapor concentrations (resulting in lower initial HO radical concentrations) led to the lower measured rate coefficients cited in the table. These data supersede those of Liu et al. (1990) at 243–298 K.

(c) HO radicals were generated by the photolysis of H_2O-O_3 mixtures at 254 nm in H_2O-O_3-CH_3CFCl_2-CH_4 (or CH_3CCl_3)-Ar-O_2 mixtures. The concentrations of CH_3CFCl_2 and CH_4 (or CH_3CCl_3) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(HO + CH_3CFCl_2)/k(HO + CH_4) = (0.49 \pm 0.16) \exp[(189 \pm 105)/T]$ and $k(HO + CH_3CFCl_2/k(HO + CH_3CCl_3) = (0.79 \pm 0.07) \exp[-(74 \pm 28)/T]$ are placed on an absolute basis by use of rate coefficients of $k(HO + CH_4) = 1.85 \times 10^{-20} T^{2.82} \exp(-987/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation) and $k(HO + CH_3CCl_3) = 2.25 \times 10^{-18} T^2 \exp(-910/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(d) Relative to $k(HO + CH_4)$.

(e) Relative to $k(HO + CH_3CCl_3)$.

Preferred Values

$k = 5.8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.1 \times 10^{-13} \exp(-1470/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-300 K.

Reliability

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

Comments on Preferred Values

The absolute rate coefficients of Brown et al. (1990) are higher than those from the absolute rate studies of Liu et al. (1990), Talukdar et al. (1991), Zhang et al. (1992), Lancar et al. (1993) and Mörs et al. (1996) at all temperatures studied, and the rate coefficients of Liu et al. (1990) at temperatures $\leq$ 298 K are significantly higher than those of Talukdar et al. (1991), Zhang et al. (1992), Lancar et al. (1993) and Mörs et al. (1996). The measurements of Zhang et al. (1992) show that the earlier lower temperature ($\leq$298 K) data of Liu et al. (1990) were in error due to the occurrence of secondary reactions of HO radicals with reaction products. The rate coefficients of Talukdar et al. (1991), Zhang et al. (1992) [obtained at low flash energies and/or low water vapor concentrations and with high associated uncertainties], Lancar et al. (1993), Mörs et al. (1996) and Huder and DeMore (1993) are in good agreement, as are those of Talukdar et al. (1991) and Liu et al. (1990) at temperatures $\geq$ 330 K.

The rate coefficients of Talukdar et al. (1991), Zhang et al. (1992), Lancar et al. (1993) and Mörs et al. (1996) have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.68 \times 10^{-18}\ T^2 \exp(-962/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 233–479 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered on a mid-range temperature, T_m, of 255 K and is obtained from the three parameter equation with $A = C\ e^2\ T_m^2$ and $B = D + 2T_m$. The rate coefficients of Huder and DeMore (1993) over the temperature range 298–358 K, obtained relative to the reactions of HO radicals with CH_4 and CH_3CCl_3, agree to within 6% with those calculated from the preferred three parameter expression.

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IV.A2.124

$HO + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.3) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
$3.72 \times 10^{-12} \exp[-(1627 \pm 50)/T]$	260-375	Watson et al., 1977	FP-RF
$(1.59 \pm 0.16) \times 10^{-14}$	298		
$1.95 \times 10^{-12} \exp[-(1331 \pm 37)/T]$	275-406	Chang and Kaufman, 1977	DF-RF
$(2.19 \pm 0.26) \times 10^{-14}$	298		
$2.4 \times 10^{-12} \exp[-(1394 \pm 113)/T]$	293-430	Clyne and Holt, 1979	DF-RF
$(1.81 \pm 0.16) \times 10^{-14}$	293		
$5.04 \times 10^{-12} \exp[-(1797 \pm 65)/T]$	278-457	Jeong and Kaufman, 1979;	DF-RF (a)
$(1.06 \pm 0.11) \times 10^{-14}$	293	Jeong et al., 1984	
$5.4 \times 10^{-12} \exp[-(1810 \pm 100)/T]$	253-363	Kurylo et al., 1979	FP-RF
$(1.08 \pm 0.20) \times 10^{-14}$	296		
$5.4 \times 10^{-12} \exp[-(1810 \pm 448)/T]$	359-402	Nelson et al., 1990	PR-RA
1.3×10^{-14}	298		
$9.1 \times 10^{-13} \exp[-(1337 \pm 150)/T]$	278-378	Finlayson-Pitts et al., 1992	DF-RF
$(1.0 \pm 0.1) \times 10^{-14}$	298		
$1.75 \times 10^{-12} \exp[-(1550 \pm 100)/T]$	233-379	Talukdar et al., 1992	PLP-LIF/FP-LIF
$(9.5 \pm 0.8) \times 10^{-15}$	298		
$2.78 \times 10^{-18} T^{2.08} \exp[-(1068 \pm 108)/T]$	298-761	Jiang et al., 1992	PLP-LIF
$(1.1 \pm 0.1) \times 10^{-14}$	298		
$(1.2 \pm 0.2) \times 10^{-14}$	298	Lancar et al., 1993	DF-EPR
Relative Rate Coefficients			
2.57×10^{-14}	298	Cox et al., 1976	RR (b)
$(9.0 \pm 0.29) \times 10^{-15}$	298 ± 3	Nelson et al., 1990	RR (c)
$1.15 \times 10^{-20} T^{2.82} \exp(-696/T)$	277-356	DeMore, 1992	RR (d)
$(1.06 \pm 0.05) \times 10^{-14}$	298		

Comments

(a) The data were also fitted to a three parameter expression, resulting in $k = 5.95 \times 10^{-20} T^{2.65} \exp[-(858 \pm 866)/T]$ cm^3 molecule^{-1} s^{-1}.

(b) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at 1.013 bar pressure. Relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based on the effect of CH_3CCl_3 on NO formation and a rate coefficient for the reaction of HO radicals with CH_4 of 6.4×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation), the rate coefficient cited in the table is obtained.

(c) HO radicals were generated by the photolysis of HONO-air mixtures at 987 mbar pressure. CH_3CCl_3 and CH_3Cl (the reference compound) were monitored during the experiments by GC. The measured rate coefficient ratio $k(HO + CH_3CCl_3)/k(HO + CH_3Cl)$ is placed on an absolute basis by use of a rate coefficient of $k(HO + CH_3Cl) = 3.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(d) HO radicals were generated by the photolysis of O_3 at 254 nm in H_2O-O_3-CH_3CCl_3-CH_4-Ar-O_2 mixtures. The concentrations of CH_3CCl_3 and CH_4 were measured by FTIR spectroscopy. The measured rate coefficient ratios of k(HO +

CH_3CCl_3)/k(HO + CH_4) = 0.62 exp(291/T) is placed on an absolute basis by use of a rate coefficient of k(HO + CH_4) = 1.85×10^{-20} $T^{2.82}$ exp(-987/T) cm^3 $molecule^{-1}$ s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 9.5 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 1.2 \times 10^{-12}$ exp(-1440/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 240–300 K.

Reliability

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

Comments on Preferred Values

The absolute rate coefficients of Finlayson-Pitts et al. (1992) and Talukdar et al. (1992) are lower than the data from the studies of Howard and Evenson (1976), Watson et al. (1977), Chang and Kaufman (1977), Clyne and Holt (1979), Jeong and Kaufman (1979), Kurylo et al. (1979), Nelson et al. (1990), Jiang et al. (1992) and Lancar et al. (1993), in part due to the presence of reactive $CH_2=CCl_2$ impurities in the CH_3CCl_3 samples used (Jeongand Kaufman, 1979; Kurylo et al., 1979) and/or the formation of $CH_2=CCl_2$ from thermal decomposition of CH_3CCl_3 on surfaces (Finlayson-Pitts et al., 1992; Talukdar et al., 1992). A unit-weighted least-squares analysis of the absolute rate coefficients of Finlayson-Pitts et al. (1992) and Talukdar et al. (1992), using the expression $k = CT^2$ exp(-D/T), leads to $k = 2.25 \times 10^{-18}$ T^2 exp(-910/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 243–379 K. The preferred Arrhenius expression, $k = A$ exp(-B/T), is centered on a mid-range temperature, T_m, of 265 K and is obtained from the three parameter equation with $A = C\, e^2\, T_m^2$ and $B = D + 2T_m$.

The relative rate coefficients of DeMore (1992) are slightly higher than the recommendation over the temperature range studied (277–356 K), by 11–15%.

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IV.A2.125

$HO + CH_2ClCF_3 \rightarrow H_2O + CHClCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.05 \pm 0.23) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
$1.1 \times 10^{-12} \exp[-(1260 \pm 60)/T]$	263-373	Handwerk and Zellner, 1978	FP-RA
$(1.5 \pm 0.3) \times 10^{-14}$	293		
$3.3 \times 10^{-11} \exp[-(2300 \pm 300)/T]$	294-427	Clyne and Holt, 1979	DF-RF
$(1.03 \pm 0.30) \times 10^{-14}$	294		
$3.06 \times 10^{-18}\, T^{1.91} \exp[-(644 \pm 313)/T]$	295-866	Fang et al., 1999	PLP-LIF
$(1.76 \pm 0.25) \times 10^{-14}$	295		

Preferred Values

$k = 1.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.6 \times 10^{-13} \exp(-1100/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260-380 K.

Reliability

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

Comments on Preferred Values

The temperature dependence of the rate coefficients obtained by Clyne and Holt (1979) is significantly higher than those measured by Handwerk and Zellner (1978) and Fang et al. (1999), and, as is the case for other haloalkanes, the data of Clyne and Holt (1979) are therefore not used in the evaluation. The rate coefficients of Fang et al. (1999) are consistently higher, by 10-20%, than those of Handwerk and Zellner over the temperature range common to both studies (295–373 K). The preferred temperature dependence is that obtained from a unit-weighted least-squares analysis of the data of Handwerk and Zellner (1978), and the preferred 298 K rate coefficient is the average of those of Howard and Evenson (1976) and Handwerk and Zellner (1978) corrected to 298 K. The pre-exponential factor is adjusted to fit the 298 K preferred rate coefficient. The temperature dependence of the rate data of Fang et al. (1999) corresponds to a value of B in the Arrhenius expression, centered on a mid-range temperature, T_m, of 300 K, of B = 1217 K, in good agreement with the recommendation.

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IV.A2.126

$HO + CH_2ClCF_2Cl \rightarrow H_2O + CHClCF_2Cl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.87 \times 10^{-12} \exp[-(1351 \pm 78)/T]$	250-350	Watson et al., 1979	FP-RF (a)
$(1.9 \pm 0.2) \times 10^{-14}$	298		
$5.54 \times 10^{-26}\, T^{4.58} \exp[-(252 \pm 377)/T]$	249-473	Jeong et al., 1984	DF-RF
$(2.42 \pm 0.16) \times 10^{-14}$	297		
$8.53 \times 10^{-19}\, T^{2.28} \exp[-(937 \pm 296)/T]$	295-788	Fang et al., 1999	PLP-LIF
$(1.84 \pm 0.07) \times 10^{-14}$	295		

Comments

(a) The sample of CH_2ClCF_2Cl used was shown by GC to contain ~0.045% of C_2 halogenated alkenes. After correction for possible contributions to the observed OH radical decays from these measured impurities, assuming a rate coefficient for reaction of the C_2 halogenated alkene impurities with HO radicals of 5×10^{-12} cm^3 molecule^{-1} s^{-1} independent of temperature, then the rate coefficient was estimated to be $3 \times 10^{-12} \exp(-1578/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range of 250–350 K, with a rate coefficient at 298 K of 1.67×10^{-14} cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k = 1.7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.5 \times 10^{-12} \exp(-1585/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The rate coefficients of Jeong et al. (1984) are higher than those of Watson et al. (1979) and Fang et al. (1999), especially at <300 K, suggesting the presence of reactive impurities in the CH_2ClCF_2Cl sample used. The rate coefficients of Jeong et al. (1984) are therefore not used in the evaluation. The rate coefficients of Fang et al. (1999) at 295 K and 347 K are in good agreement with the corrected data of Watson et al. (1979) at 298 K and 350 K (see Comment (a) above). Accordingly, the absolute rate coefficients of Watson et al. (1979) [corrected for the impurity observed; see Comment (a)] and Fang et al. (1999) have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 5.72 \times 10^{-18}\, T^2 \exp(-1006/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–788 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered on a mid-range temperature, T_m, of 290 K and is obtained from the three parameter equation with $A = C\, e^2\, T_m^2$ and $B = D + 2T_m$.

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IV.A2.127

$HO + CHFClCF_3 \rightarrow H_2O + CFClCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.24 \pm 0.19) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
6.13×10^{-13} exp[-(1244 ± 90)/T]	250-375	Watson et al., 1979	FP-RF
$(9.4 \pm 0.3) \times 10^{-15}$	301		
4.45×10^{-13} exp[-(1150 ± 60)/T]	210-349	Gierczak et al., 1991	DF-LMR/FP-RF
$(9.44 \pm 0.75) \times 10^{-15}$	298		(a)
7.72×10^{-20} $T^{2.35}$ exp[-(458 ± 30)/T]	297-867	Yamada et al., 2000	PLP-LIF
$(1.08 \pm 0.16) \times 10^{-14}$	297		
Relative Rate Coefficients			
6.48×10^{-21} $T^{2.82}$ exp[-(620 ± 40)/T]	298-366	Hsu and DeMore, 1995	RR (b,c)
7.68×10^{-15}	298		
8.28×10^{-19} T^2exp[-(674 ± 52)/T]	298-356	Hsu and DeMore, 1995	RR (b,d)
7.66×10^{-15}	298		

Comments

(a) Rate coefficients were measured over the temperature range 210–425 K. Those at the highest temperatures (400 K and 425 K) are higher than extrapolation of the linear Arrhenius plot obtained from the 210–349 K data.

(b) HO radicals were generated by the photolysis of H_2O at 185 nm or from O_3-H_2O mixtures in the UV, in H_2O (or H_2O-O_3)-$CHFClCF_3$-CH_4 (or CHF_2CHF_2)-O_2-N_2 mixtures. The concentrations of $CHFClCF_3$ and CH_4 (or CHF_2CHF_2) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(HO + CHFClCF_3)/k(HO + CH_4) = (0.35 \pm 0.04)$ exp[(367 ± 40)/T] and $k(HO + CHFClCF_3)/k(HO + CHF_2CHF_2) = (0.46 \pm 0.07)$ exp[(300 ± 52)/T] are placed on an absolute basis by using rate coefficients of $k(HO + CH_4) = 1.85 \times 10^{-20}\ T^{2.82}$ exp(-987/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation) and $k(HO + CHF_2CHF_2) = 1.80 \times 10^{-18}\ T^2$ exp(-974/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) Relative to $k(HO + CH_4)$.

(d) Relative to $k(HO + CHF_2CHF_2)$.

Preferred Values

$k = 8.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.5 \times 10^{-13}$ exp(-1105/T) cm^3 molecule^{-1} s^{-1} over the temperature range 210–300 K.

Reliability

$\Delta \log k = \pm 0.20$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

At room temperature, the absolute and relative rate coefficients of Howard and Evenson (1976), Watson et al. (1979), Gierczak et al. (1991), Hsu and DeMore (1995) and Yamada et al. 2000) range over a factor of ∼1.6, with the absolute rate coefficient of Howard and Evenson (1976) being the highest, possibly due to the presence of reactive impurities. The absolute rate coefficients of Yamada et al. (2000) are slightly higher than those of Watson et al. (1979) and Gierczak et al. (1991) over the temperature ranges common to these studies (295–375 K and 295–425 K, respectively), with the differences decreasing as the temperature increases [and with the 425 K rate coefficient of Gierczak et al. (1991) being very consistent with the 415 K and 438 K rate coefficients of Yamada et al. (2000)]. The relative rate coefficients of Hsu and DeMore (1995), using both CH_4 and CHF_2CHF_2 as reference compounds, are consistently lower than the absolute rate coefficients of Watson et al. (1979) and Gierczak et al. (1991), by ∼15-20% at 298 K. The rate coefficients of Watson et al. (1979), Gierczak et al. (1991) and Hsu and DeMore (1995) have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 7.47 \times 10^{-19} T^2 \exp(-606/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210–425 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered on a mid-range temperature, T_m, of 250 K and is derived from the three parameter equation with $A = C\ e^2\ T_m^2$ and $B = D + 2T_m$. The temperature dependence obtained by Yamada et al. (2000) is in good agreement with the recommendation, corresponding to a value of B in an Arrhenius expression centered at 250 K of B = 1046 K.

References

Gierczak, T., Talukdar, R., Vaghjiani, G. L., Lovejoy, E. R. and Ravishankara, A. R.: J. Geophys. Res., 96, 5001, 1991.
Howard, C. J. and Evenson, K. M.: J. Chem. Phys., 64, 4303, 1976.
Hsu, K.-J. and DeMore, W. B.: J. Phys. Chem., 99, 1235, 1995.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Watson, R. T., Ravishankara, A. R., Machado, G., Wagner, S. and Davis, D. D.: Int. J. Chem. Kinet, 11, 187, 1979.
Yamada, T., Fang, T. D., Taylor, P. H. and Berry, R. J.: J. Phys. Chem. A, 104, 5013, 2000.

IV.A2.128

$HO + CHCl_2CF_3 \rightarrow H_2O + CCl_2CF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.84 \pm 0.43) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
1.24×10^{-12} exp[-(1056 ± 70)/T]	245-375	Watson et al., 1979	FP-RF (a)
$(3.6 \pm 0.4) \times 10^{-14}$	298		
1.12×10^{-12} exp[-(1000 ± 100)/T]	293-429	Clyne and Holt, 1979	DF-RF
$(3.86 \pm 0.19) \times 10^{-14}$	293		
1.1×10^{-12} exp[-(1040 ± 140)/T]	270-400	Liu et al., 1990	FP-RF
$(3.52 \pm 0.28) \times 10^{-14}$	298		
1.18×10^{-12} exp[-(900 ± 150)/T]	232-426	Brown et al., 1990	DF-RF
$(5.9 \pm 0.6) \times 10^{-14}$	303		
6.5×10^{-13} exp[-(840 ± 40)/T]	213-322	Gierczak et al., 1991	DF-LMR/FP-RF (b)
$(3.69 \pm 0.37) \times 10^{-14}$	298		
1.1×10^{-12} exp[-(940 ± 200)/T]	295-385	Nielsen, 1991	PR-RA
$(4.3 \pm 1.0) \times 10^{-14}$	295		
2.20×10^{-19} $T^{2.88}$ exp[-(226 ± 51)/T]	296-866	Yamada et al., 2000	PLP-LIF
$(3.67 \pm 0.24) \times 10^{-14}$	296.3		
Relative Rate Coefficients			
7.84×10^{-19} T^2 exp[-(215 ± 36)/T]	298-359	Hsu and DeMore, 1995	RR (c)
3.38×10^{-14}	298		

Comments

(a) The sample of $CHCl_2CF_3$ used was shown by GC to contain 0.0227% of $C_4F_5HCl_2$ and 0.0021% of C_4F_6HCl. After correction for possible contributions to the observed OH radical decays from these measured impurities, assuming a rate coefficient for reaction of the halogenated alkene impurities with HO radicals of 5×10^{-12} cm^3 molecule^{-1} s^{-1} independent of temperature, then the rate coefficient was estimated to be 1.4×10^{-12} exp(-1102/T) cm^3 molecule^{-1} s^{-1} over the temperature range of 245–375 K, with a rate coefficient at 298 K of 3.49×10^{-14} cm^3 molecule^{-1} s^{-1}.

(b) Rate coefficients were measured over the temperature range 213–380 K.

(c) HO radicals were generated by the photolysis of H_2O at 185 nm or O_3 at 254 nm in the presence of H_2O, in H_2O (or H_2O-O_3)-$CHCl_2CF_3$-CH_3CHF_2-O_2-N_2 mixtures. The concentrations of $CHCl_2CF_3$ and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CHCl_2CF_3)/k(HO + CH_3CHF_2) = (0.28 \pm 0.03)$ exp[(365 ± 36)/T] is placed on an absolute basis by using a rate coefficient of $k(HO + CH_3CHF_2) = 2.80 \times 10^{-18}$ T^2 exp(-580/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 3.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.6 \times 10^{-13}$ exp(-870/T) cm^3 molecule^{-1} s^{-1} over the temperature range 210-300 K.

Reliability

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

Comments on Preferred Values

The absolute rate coefficients of Howard and Evenson (1976), Watson et al. (1979) [corrected for impurities; see Comment (a)], Clyne and Holt (1979), Liu et al. (1990), Gierczak et al. (1991) and Yamada et al. (2000) and the relative rate coefficients of Hsu and DeMore (1995) are in reasonable agreement, but are significantly lower than the absolute rate coefficients of Brown et al. (1990) and Nielsen (1991). The absolute rate coefficients of Yamada et al. (2000) tend to be slightly higher than those of Watson et al. (1979) [corrected for impurities], Liu et al. (1990) and Gierczak et al. (1991), while the relative rate coefficients of Hsu and DeMore (1995) tend to be slightly lower. Although in this case the data of Clyne and Holt (1979) are in good agreement with the studies of Howard and Evenson (1976), Watson et al. (1979), Liu et al. (1990), Gierczak et al. (1991) and Yamada et al. (2000), because of discrepancies between their data and those of other investigators for most other haloalkanes studied, the data of Clyne and Holt (1979) have not been used in the evaluation. The rate coefficients of Howard and Evenson (1976), Watson et al. (1979) [corrected for impurities; see Comment (a)], Liu et al. (1990), Gierczak et al. (1991), Yamada et al. (2000) and Hsu and DeMore (1995) have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.42 \times 10^{-18}\ T^2 \exp(-370/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 213–866 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered on a mid-range temperature, T_m, of 250 K and is obtained from the three parameter equation with $A = C\ e^2\ T_m^2$ and $B = D + 2T_m$.

References

Brown, A. C., Canosa-Mas, C. E., Parr, A. D. and Wayne, R. P.: Atmos. Environ., 24A, 2499, 1990.
Clyne, M. A. A. and Holt, P. M.: J. Chem. Soc. Faraday Trans. 2, 75, 582, 1979.
Gierczak, T., Talukdar, R., Vaghjiani, G. L., Lovejoy, E. R. and Ravishankara, A. R.: J. Geophys. Res., 96, 5001, 1991.
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Nielsen, O. J.: Chem. Phys. Lett., 187, 286, 1991.
Watson, R. T., Ravishankara, A. R., Machado, G., Wagner, S. and Davis, D. D.: Int. J. Chem. Kinet., 11, 187, 1979.
Yamada, T., Fang, T. D., Taylor, P. H. and Berry, R. J.: J. Phys. Chem. A, 104, 5013, 2000.

IV.A2.129

$HO + CHFClCF_2Cl \rightarrow H_2O + CFClCF_2Cl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$9.2 \times 10^{-13} \exp[-(1281 \pm 85)/T]$	298-460	Orkin and Khamaganov, 1993	DF-EPR
$(1.23 \pm 0.10) \times 10^{-14}$	298		

Preferred Values

$k = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.4 \times 10^{-13} \exp(-1255/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290-460 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred Arrhenius expression is obtained from a unit-weighted least-squares analysis of the absolute rate coefficients of Orkin and Khamaganov (1993), the sole study conducted to date.

References

Orkin, V. L. and Khamaganov, V. G.: J. Atmos. Chem., 16, 157, 1993.

IV.A2.130

$HO + CHCl_2CF_2Cl \rightarrow H_2O + CCl_2CF_2Cl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.13 \times 10^{-12} \exp[-(918 \pm 52)/T]$	298-460	Orkin and Khamaganov, 1993	DF-EPR
$(5.30 \pm 0.41) \times 10^{-14}$	298		
Relative Rate Coefficients			
$9.0 \times 10^{-13} \exp[-(868 \pm 32)/T]$	303-363	DeMore, 1996	RR (a,b)
4.87×10^{-14}	298*		
$1.36 \times 10^{-18}\ T^2 \exp[-(256 \pm 98)/T]$	313-371	DeMore, 1996	RR (a,c)
5.12×10^{-14}	298*		

Comments

(a) HO radicals were generated by the photolysis of H_2O at 185 nm or O_3 at 254 nm in the presence of H_2O, in H_2O (or H_2O-O_3)-$CHCl_2CF_2Cl$-CH_2Cl_2 (or $CHCl_2CF_3$)-O_2-N_2 mixtures. The concentrations of $CHCl_2CF_2Cl$ and CH_2Cl_2 (or $CHCl_2CF_3$) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(HO + CHCl_2CF_2Cl)/k(HO + CH_2Cl_2) = (0.50 \pm 0.05) \exp[-(8 \pm 32)/T]$ and $k(HO + CHCl_2CF_2Cl)/k(HO + CHCl_2CF_3) = (0.96 \pm 0.28) \exp[(114 \pm 98)/T]$ are placed on an absolute basis by using rate coefficients of $k(HO + CH_2Cl_2) = 1.8 \times 10^{-12} \exp(-860/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation) and $k(HO + CHCl_2CF_3) = 1.42 \times 10^{-18}\ T^2 \exp(-370/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) Relative to $k(HO + CH_2Cl_2)$.

(c) Relative to $k(HO + CHCl_2CF_3)$.

Preferred Values

$k = 5.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.1 \times 10^{-13} \exp(-825/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270-340 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

Over the temperature range 298–371 K, the absolute rate coefficients of Orkin and Khamaganov (1993) and the relative rate coefficients of DeMore (1996), using both CH_2Cl_2 and $CHCl_2CF_3$ as reference compounds, are in good agreement. Accordingly, the three parameter equation $k = CT^2 \exp(-D/T)$ was fitted to the rate coefficients of Orkin and Khamaganov (1993) and DeMore (1996), resulting in $k = 1.23 \times 10^{-18}\ T^2 \exp(-227/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 298–460 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered on a mid-range temperature, T_m, of 300 K and is obtained from the three parameter equation with $A = C\ e^2\ T_m^2$ and $B = D + 2T_m$.

References

DeMore, W. B.: J. Phys. Chem., 100, 5813, 1996.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Orkin, V. L. and Khamaganov, V. G.: J. Atmos. Chem., 16, 157, 1993.

IV.A2.131

$HO + CHFClCFCl_2 \rightarrow H_2O + CFClCFCl_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$8.68 \times 10^{-19}\ T^2 \exp[-(463 \pm 42)/T]$	294-362	Hsu and DeMore, 1995	RR (a)
1.63×10^{-14}	298		

Comments

(a) HO radicals were generated by the photolysis of H_2O at 185 nm or O_3 at 254 nm in the presence of H_2O, in H_2O (or H_2O-O_3)-$CHFClCFCl_2$-CH_3CHF_2-O_2-N_2 mixtures. The concentrations of $CHFClCFCl_2$ and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + $CHFClCFCl_2$/k(HO + CH_3CHF_2) = (0.31 ± 0.04) exp[(117 ± 42)/T] is placed on an absolute basis by using a rate coefficient of k(HO + CH_3CHF_2) = $2.80 \times 10^{-18}\ T^2$ exp(-580/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.8 \times 10^{-13} \exp(-1065/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270-340 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred values are based on the relative rate coefficients of Hsu and DeMore (1995), the sole study conducted to date. The preferred Arrhenius expression $k = A \exp(-B/T)$ is centered on a mid-range temperature, T_m, of 300 K and is derived from the cited three parameter expression, $k = CT^2 \exp(-D/T)$, with $A = C\, e^2\, T_m^2$ and $B = D + 2T_m$.

References

Hsu, K.-J. and DeMore, W. B.: J. Phys. Chem., 99, 1235, 1995.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.

IV.A2.132

$HO + CHCl_2CF_2CF_3 \rightarrow H_2O + CCl_2CF_2CF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.3 \times 10^{-13} \exp[-(550 \pm 750)/T]$	251-393	Brown et al., 1990	DF-RF
$(3.7 \pm 0.8) \times 10^{-14}$	300		
$1.92 \times 10^{-12} \exp[-(1290 \pm 90)/T]$	270-400	Zhang et al., 1991	FP-RF
$(2.60 \pm 0.29) \times 10^{-14}$	298		
$6.5 \times 10^{-13} \exp[-(970 \pm 115)/T]$	295-364	Nelson et al., 1992	DF-LIF
$(2.41 \pm 0.24) \times 10^{-14}$	295		

Preferred Values

$k = 2.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.1 \times 10^{-12} \exp(-1130/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270-400 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The rate coefficients measured by Zhang et al. (1991) and Nelson et al. (1992) over the temperature range 295–365 K are in good agreement within the experimental uncertainties. The rate coefficients measured by Brown et al. (1990) at 251 K and 300 K are significantly higher, and are not used in the evaluation. The preferred 298 K rate coefficient is the average of those calculated from the Arrhenius expressions of Zhang et al. (1991) and Nelson et al. (1992), and the preferred temperature dependence is the mean of those of Zhang et al. (1991) and Nelson et al. (1992) [a least-squares analysis of the rate coefficients of Zhang et al. (1991) and Nelson et al. (1992) yields $k = 1.56 \times 10^{-12} \exp(-1239/T)$ cm^3 molecule^{-1} s^{-1}, largely weighted by the 270 K and 400 K rate coefficients of Zhang et al. (1991)]. The pre-exponential factor is adjusted to fit the preferred 298 K rate coefficient and the temperature dependence.

References

Brown, A. C., Canosa-Mas, C. E., Parr, A. D., Rothwell, K. and Wayne, R. P.: Nature, 347, 541, 1990.
Nelson, D. D. Jr., Zahniser, M. S. and Kolb, C. E.: J. Phys. Chem., 96, 249, 1992.
Zhang, Z., Liu, R., Huie, R. E. and Kurylo, M. J.: Geophys. Res. Lett., 18, 5, 1991.

IV.A2.133

$HO + CHFClCF_2CF_2Cl \rightarrow H_2O + CFClCF_2CF_2Cl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$6.75 \times 10^{-13} \exp[-(1300 \pm 180)/T]$	298-400	Zhang et al., 1991	FP-RF
$(8.6 \pm 1.1) \times 10^{-15}$	298		
$3.9 \times 10^{-13} \exp[-(1120 \pm 125)/T]$	295-374	Nelson et al., 1992	DF-LIF
$(9.0 \pm 1.1) \times 10^{-15}$	295		

Preferred Values

$k = 8.9 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.5 \times 10^{-13} \exp(-1230/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290-400 K.

Reliability

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

Comments on Preferred Values

The preferred values are derived from a least-squares analysis of the rate coefficients of Zhang et al. (1991) and Nelson et al. (1992), which are in excellent agreement.

References

Nelson, D. D. Jr., Zahniser, M. S. and Kolb, C. E.: J. Phys. Chem., 96, 249, 1992.
Zhang, Z., Liu, R., Huie, R. E. and Kurylo, M. J.: Geophys. Res. Lett., 18, 5, 1991.

IV.A2.134

$HO + CH_3CF_2CFCl_2 \rightarrow H_2O + CH_2CF_2CFCl_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
7.1×10^{-13} exp[-(1690 ± 230)/T]	295-367	Nelson et al., 1992	DF-LIF
(2.1 ± 0.2) × 10^{-15}	295		

Preferred Values

$k = 2.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.0 \times 10^{-13}$ exp(-1690/T) cm^3 molecule^{-1} s^{-1} over the temperature range 290-370 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are based on the sole study of Nelson et al. (1992).

References

Nelson, D. D. Jr., Zahniser, M. S. and Kolb, C. E.: J. Phys. Chem., 96, 249, 1992.

IV.A2.135

$HO + HC(O)Cl \rightarrow H_2O + ClCO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$\leq 3.2 \times 10^{-13}$	299.2	Libuda et al., 1990	RR (a)

Comments

(a) HO radicals were generated by the thermal decomposition of HO_2NO_2 after addition of NO to HC(O)Cl-n-butane-HO_2NO_2-O_2-N_2 mixtures at 800 mbar pressure. The concentrations of HC(O)Cl and n-butane were monitored by FTIR spectroscopy and GC, respectively. No decay of HC(O)Cl was observed, leading to the upper limit to the rate coefficient cited in the table.

Preferred Values

$k < 5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the upper limit to the rate coefficient reported by Libuda et al. (1990).

References

Libuda, H. G., Zabel, F., Fink, E. H. and Becker, K. H.: J. Phys. Chem., 94, 5860, 1990.

IV.A2.136

HO + $CH_3OCl \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.4 \times 10^{-12} \exp[-(360 \pm 100)/T]$	250-341	Crowley et al., 1996	PLP-RF (a)
$(7.06 \pm 0.22) \times 10^{-13}$	294		

Comments

(a) HO radicals were generated from the pulsed laser photolysis of HNO_3 at 248 nm. CH_3OCl-Ar samples were shown to be stable with respect to decomposition over long time periods (up to 3 months). Each CH_3OCl-Ar sample used was analyzed for Cl_2 impurities by UV absorption before entering the reaction cell. At 294 K, no effect of total pressure of argon diluent (40–400 mbar) on the measured rate coefficient was observed, and the weighted average 294 K rate coefficient is given in the table.

Preferred Values

$k = 7.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.4 \times 10^{-12} \exp(-360/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are based on the sole study of this reaction by Crowley et al. (1996). The products have not been measured to date, but formation of $H_2O + CH_2OCl$ and $HOCl + CH_3O$ are possible.

References

Crowley, J. N., Campuzano-Jost, P. and Moortgat, G. K.: J. Phys. Chem. 100, 3601, (1996).

IV.A2.137

HO + C(O)Cl_2 → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$<1 \times 10^{-15}$	298 ± 3	Nelson et al., 1990	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in CH_3ONO-NO-C(O)Cl_2-reference compound-air mixtures at ∼1 bar pressure. The concentrations of C(O)Cl_2 and the reference compound were monitored during the experiments by GC. No reaction of C(O)Cl_2 was observed. However, no details concerning the reference compound used or the amount of reference compound reacted were given.

Preferred Values

$k < 5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit to the 298 K rate coefficient is based on the sole reported study of Nelson et al. (1990), with the preferred upper limit being increased by a factor of 5 over that cited by Nelson et al. (1990).

References

Nelson, L., Shanahan, I., Sidebottom, H. W., Treacy, J. and Nielsen, O. J.: Int. J. Chem. Kinet., 22, 577, 1990.

IV.A2.138

$$\begin{aligned} \mathbf{HO + CH_2ClCHO} &\rightarrow \mathbf{H_2O + CH_2ClCO} \quad &(1)\\ &\rightarrow \mathbf{H_2O + CHClCHO} \quad &(2) \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.0 \pm 0.6) \times 10^{-12}$	298	Balestra-Garcia et al., 1992	PLP-RF
Relative Rate Coefficients			
$(3.2 \pm 0.2) \times 10^{-12}$	298 ± 2	Scollard et al., 1993	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO or C_2H_5ONO in CH_3ONO (or C_2H_5ONO)-NO-CH_2ClCHO-$CH_3C(O)CH_2CH_3$-air mixtures at 987 ± 13 mbar pressure. The concentrations of CH_2ClCHO and 2-butanone were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of k(HO + CH_2ClCHO)/k(HO + 2-butanone) is placed on an absolute basis by use of a rate coefficient of k(HO + 2-butanone) = 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

Preferred Values

$k = 3.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of those of Balestra-Garcia et al. (1992) and Scollard et al. (1993), which are in excellent agreement. The reaction is expected to proceed essentially totally by channel (1) at 298 K.

References

Balestra-Garcia, C., Le Bras, G. and Mac Leod, H.: J. Phys. Chem., 96, 3312, 1992.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Scollard, D. J., Treacy, J. J., Sidebottom, H. W., Balestra-Garcia, C., Laverdet, G., LeBras, G., MacLeod, H. and Téton, S.: J. Phys. Chem., 97, 4683, 1993.

IV.A2.139

$$\mathbf{HO + CHFClCHO} \rightarrow \mathbf{H_2O + CHFClCO} \quad \mathbf{(1)}$$
$$\rightarrow \mathbf{H_2O + CFClCHO} \quad \mathbf{(2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.2) \times 10^{-12}$	298 ± 2	Scollard et al., 1993	PLP-RF
Relative Rate Coefficients			
$(1.9 \pm 0.3) \times 10^{-12}$	298 ± 2	Scollard et al., 1993	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO or C_2H_5ONO in CH_3ONO (or C_2H_5ONO)-CHFClCHO-toluene-air mixtures at 987 ± 13 mbar pressure. The concentrations of CHFClCHO and toluene were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of k(HO + CHFClCHO)/k(HO + toluene) is placed on an absolute basis by using a rate coefficient of k(HO + toluene) = 5.63×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Calvert et al., 2002).

Preferred Values

$k = 2.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is an average of the absolute and relative rate coefficients of Scollard et al. (1993), which are in good agreement. The reaction is expected to proceed by channel (1) at room temperature (Scollard et al., 1993).

References

Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J. and Yarwood, G.: The Mechanism of Atmospheric Oxidation of Aromatic Hydrocarbons, Oxford University Press, New York, NY, 2002.
Scollard, D. J., Treacy, J. J., Sidebottom, H. W., Balestra-Garcia, C., Laverdet, G., LeBras, G., MacLeod, H. and Téton, S.: J. Phys. Chem., 97, 4683, 1993.

IV.A2.140

$$\begin{aligned} \mathbf{HO + CHCl_2CHO} &\rightarrow \mathbf{H_2O + CHCl_2CO} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{H_2O + CCl_2CHO} \quad \mathbf{(2)} \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.4 \pm 0.5) \times 10^{-12}$	298	Balestra-Garcia et al., 1992	PLP-RF
Relative Rate Coefficients			
$(2.4 \pm 0.1) \times 10^{-12}$	298 ± 2	Scollard et al., 1993	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO or C_2H_5ONO in CH_3ONO (or C_2H_5ONO)-NO-$CHCl_2CHO$-$CH_3C(O)CH_2CH_3$-air mixtures at 987 ± 13 mbar pressure. The concentrations of $CHCl_2CHO$ and 2-butanone were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of k(HO + $CHCl_2CHO$)/k(HO + 2-butanone) is placed on an absolute basis by use of a rate coefficient of k(HO + 2-butanone) = 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

Preferred Values

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

Reliability

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

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of those of Balestra-Garcia et al. (1992) and Scollard et al. (1993), which are in excellent agreement. The reaction is expected to proceed essentially totally by channel (1) at 298 K (Scollard et al., 1993).

References

Balestra-Garcia, C., Le Bras, G. and Mac Leod, H. : J. Phys. Chem., 96, 3312, 1992.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Scollard, D. J., Treacy, J. J., Sidebottom, H. W., Balestra-Garcia, C., Laverdet, G., LeBras, G., MacLeod, H. and Téton, S.: J. Phys. Chem., 97, 4683, 1993.

IV.A2.141

$HO + CF_2ClCHO \rightarrow H_2O + CF_2ClCO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.5 \pm 0.5) \times 10^{-13}$	298 ± 2	Scollard et al., 1993	PLP-RF
Relative Rate Coefficients			
$(6.9 \pm 0.5) \times 10^{-13}$	298 ± 2	Scollard et al., 1993	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO or C_2H_5ONO in CH_3ONO (or C_2H_5ONO)-CF_2ClCHO-ethanol-air mixtures at 987 ± 13 mbar pressure. The concentrations of CF_2ClCHO and ethanol were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CF_2ClCHO)/k(HO + \text{ethanol})$ is placed on an absolute basis by using a rate coefficient of $k(HO + \text{ethanol}) = 3.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

Preferred Values

$k = 8.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is an average of the absolute and relative rate coefficients of Scollard et al. (1993), which are in reasonable agreement.

References

IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
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IV.A2.142

$HO + CFCl_2CHO \rightarrow H_2O + CFCl_2CO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.3 \pm 0.1) \times 10^{-12}$	298 ± 2	Scollard et al., 1993	PLP-RF
Relative Rate Coefficients			
$(1.0 \pm 0.2) \times 10^{-12}$	298 ± 2	Scollard et al., 1993	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO or C_2H_5ONO in CH_3ONO (or C_2H_5ONO)-$CFCl_2CHO$-toluene-air mixtures at 987 ± 13 mbar pressure. The concentrations of $CFCl_2CHO$ and toluene were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CFCl_2CHO)/k(HO + \text{toluene})$ is placed on an absolute basis by using a rate coefficient of $k(HO + \text{toluene}) = 5.63 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Calvert et al., 2002).

Preferred Values

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

Reliability

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

Comments on Preferred Values

The preferred value is an average of the absolute and relative rate coefficients of Scollard et al. (1993), which are in good agreement.

References

Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J. and Yarwood, G.: The Mechanism of Atmospheric Oxidation of Aromatic Hydrocarbons, Oxford University Press, New York, NY, 2002.

Scollard, D. J., Treacy, J. J., Sidebottom, H. W., Balestra-Garcia, C., Laverdet, G., LeBras, G., MacLeod, H. and Téton, S.: J. Phys. Chem., 97, 4683, 1993.

IV.A2.143

$HO + CCl_3CHO \rightarrow H_2O + CCl_3CO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.25 \times 10^{-11} \exp[-(600 \pm 90)/T]$	298-520	Dóbé et al., 1989	DF-RF/LIF
$(1.56 \pm 0.34) \times 10^{-12}$	298		
$(8.7 \pm 1.7) \times 10^{-13}$	298	Balestra-Garcia et al., 1992	PLP-RF
$(1.28 \pm 0.25) \times 10^{-12}$	298 ± 2	Barry et al., 1994	DF-RF
$(8.9 \pm 1.5) \times 10^{-13}$	298 ± 2	Barry et al., 1994	DF-EPR
$1.79 \times 10^{-12} \exp[-(240 \pm 60)/T]$	233-415	Talukdar et al., 2001	PLP-LIF
$(8.3 \pm 0.8) \times 10^{-13}$	298		
Relative Rate Coefficients			
$(1.63 \pm 0.29) \times 10^{-12}$	298 ± 3	Nelson et al., 1990	RR (a)
$(1.5 \pm 0.2) \times 10^{-12}$	298 ± 2	Scollard et al., 1993	RR (b)
$(9.5 \pm 0.3) \times 10^{-13}$	298 ± 2	Barry et al., 1994	RR (c)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in CH_3ONO-CCl_3CHO-ethyl acetate (the reference compound)-air mixtures at 987 mbar pressure, and NO and ethene were added to the reactant mixtures to scavenge Cl atoms formed from the photolysis of CCl_3CHO. The concentrations of CCl_3CHO and ethyl acetate were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of k(HO + CCl_3CHO)/k(HO + ethyl acetate) is placed on an absolute basis by using a rate coefficient of k(HO + ethyl acetate) = 1.6×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson, 1989).

(b) HO radicals were generated by the photolysis of CH_3ONO or C_2H_5ONO in CH_3ONO (or C_2H_5ONO)-CCl_3CHO-toluene-air mixtures at 987 ± 13 mbar pressure. The concentrations of CCl_3CHO and toluene were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of k(HO + CCl_3CHO)/k(HO + toluene) is placed on an absolute basis by using a rate coefficient of k(HO + toluene) = 5.63×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Calvert et al., 2002).

(c) HO radicals were generated by the photolysis of O_3 in the presence of water vapor in O_3-H_2O-CCl_3CHO-2-methylpropane-air mixtures at ∼1 bar pressure. The concentrations of CCl_3CHO and 2-methylpropane were measured by GC. The measured rate coefficient ratio k(HO + CCl_3CHO)/k(HO + 2-methylpropane) = 0.45 ± 0.01 is placed on an absolute basis by using a rate coefficient of k(HO + 2-methylpropane) = 2.12×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

Preferred Values

$k = 8.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.8 \times 10^{-12} \exp(-240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-420 K.

Reliability

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

Comments on Preferred Values

The absolute and relative rate study of Barry et al. (1994) supersedes the earlier studies of Nelson et al. (1990), Balestra-Garcia et al. (1992) and Scollard et al. (1993). The three independent determinations of the rate coefficient by Barry et al. (1994) are all lower than the absolute 298 K rate coefficient of Dóbé et al. (1989), as is the most recent absolute room temperature rate coefficient of Talukdar et al. (2001). The most recent and extensive study of Talukdar et al. (2001) obtains a room temperature rate coefficient which agrees with the lowest of the previously reported 298 K rate coefficients, these being the PLP-RF rate coefficient of Balestra-Garcia et al. (1992) and the DF-EPR rate coefficient of Barry et al. (1994). The temperature dependence of the rate coefficient measured by Talukdar et al. (2001) is also significantly smaller than that reported by Dóbé et al. (1989). The potential exists for erroneously high measured rate coefficients because of secondary reactions involving Cl atoms generated from the photolysis of CCl_3CHO, as well as for erroneously low measured rate coefficients because of wall adsorption losses of CCl_3CHO. The concentrations of CCl_3CHO were measured by UV absorption at 213.9 nm before and after the reaction cell in the Talukdar et al. (2001) study, and losses were shown to be of no importance ($<2\%$). The preferred values are therefore based on the absolute rate coefficients of Talukdar et al. (2001).

References

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IV.A2.144

$HO + CH_3C(O)Cl \rightarrow H_2O + CH_2COCl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
6.8×10^{-14}	298 ± 3	Nelson et al., 1984; 1990	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in CH_3ONO-NO-$CH_3C(O)Cl$-$CHCl_3$ (the reference compound)-air mixtures at 987 mbar pressure. The concentrations of $CH_3C(O)Cl$ and $CHCl_3$ were monitored during the experiments by GC. The measured rate coefficient ratio of $k(HO + CH_3C(O)Cl)/k(HO + CHCl_3) \sim 0.65$ is placed on an absolute basis by use of a rate coefficient of $k(HO + CHCl_3) = 1.05 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

Preferred Values

$k = 6.8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the relative rate coefficient studies of Nelson et al. (1984) and Nelson et al. (1990), using the data presented in Table I and Figure 2 of Nelson et al. (1984) and in Figure 5 of Nelson et al. (1990), which are the same data-set. Note that Table I of Nelson et al. (1990) cites a rate coefficient a factor of 7 lower [$(9.1 \pm 3.2) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 ± 3 K], inconsistent with the data presented in their Figure 5 and with the data presented in Nelson et al. (1984).

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Nelson, L., Shanahan, I., Sidebottom, H. W., Treacy, J. and Nielsen, O. J.: Int. J. Chem. Kinet., 22, 577, 1990.

IV.A2.145

$$\mathbf{HO + CHF_2OCHClCF_3 \rightarrow H_2O + CHF_2OCClCF_3 \quad (1)}$$
$$\mathbf{\rightarrow H_2O + CF_2OCHClCF_3 \quad (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.7) \times 10^{-14}$	298	Brown et al., 1989; 1990	DF-RF
1.12×10^{-12} exp[-(1280 ± 50)/T]	250-430	Tokuhashi et al., 1999	PLP/FP/DF-LIF
$(1.51 \pm 0.05) \times 10^{-14}$	298		
$(1.7 \pm 0.3) \times 10^{-14}$	298	Langbein et al., 1999	PLP-UVA
4.5×10^{-13} exp[-(940 ± 100)/T]	293-393	Beach et al., 2001	DF-RF
$(1.9 \pm 0.2) \times 10^{-14}$	293		
Relative Rate Coefficients			
$<3 \times 10^{-13}$	300 ± 3	McLoughlin et al., 1993	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-$CHF_2OCHClCF_3$-diethyl ether air mixtures at ∼1 bar pressure. The concentrations of $CHF_2OCHClCF_3$ and diethyl ether were measured by GC. The measured upper limit to the rate coefficient ratio k(HO + $CHF_2OCHClCF_3$)/k(HO + diethyl ether) is placed on an absolute basis by using a rate coefficient of k(HO + diethyl ether) = 1.31×10^{-11} cm^3 molecule^{-1} s^{-1} at 300 K (Atkinson, 1994).

Preferred Values

$k = 1.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.1 \times 10^{-12}$ exp(-1280/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250-430 K.

Reliability

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

Comments on Preferred Values

The study of Tokuhashi et al. (1999) used samples of $CHF_2OCHClCF_3$ purified by GC (99.999% purity as analyzed by GC), and the 298 K rate coefficients obtained using three independent techniques (PLP-LIF, FP-LIF and DF-LIF) were identical within the experimental errors. The room temperature rate coefficients of Brown et al. (1989; 1990) are higher than the rate coefficient of Tokuhashi et al. (1999), possibly in part because of the presence of reactive impurities in the CHF_2OCF_2CHFCl sample used by Brown et al. (1989, 1990) [see Tokuhashi et al. (1999)]. The rate coefficients of Beach et al. (2001) at 360 K and 393 K are in excellent agreement with the data of Tokuhashi et al. (1999). However, the 293 K rate coefficient of Beach et al. (2001) is 25% higher than the 298 K rate coefficient of Tokuhashi et al. (1999), which is in agreement with the absolute rate coefficient of Langbein et al. (1999). The preferred values are those of Tokuhashi et al. (1999), with the uncertainty in the value of E/R being sufficient to encompass the temperature dependence reported by Beach et al. (2001). The upper limit to the rate coefficient measured by McLoughlin et al. (1993) is consistent with the preferred values.

References

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McLoughlin, P., Kane, R. and Shanahan, I.: Int. J. Chem. Kinet., 25, 137, 1993.
Tokuhashi, K., Takahashi, A., Kaise, M. and Kondo, S.: J. Geophys. Res., 104, 18681, 1999.

IV.A2.146

$$\mathbf{HO + CHF_2OCF_2CHFCl \rightarrow H_2O + CHF_2OCF_2CFCl \quad (1)}$$
$$\mathbf{\rightarrow H_2O + CF_2OCF_2CHFCl \quad (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.7 \pm 0.5) \times 10^{-14}$	302	Brown et al., 1989; 1990	DF-RF
$(4.7 \pm 0.7) \times 10^{-14}$	422		
7.46×10^{-13} exp[-(1230 ± 80)/T]	250-430	Tokuhashi et al., 1999	PLP/FP/DF-LIF
$(1.19 \pm 0.06) \times 10^{-14}$	298		
$(1.2 \pm 0.2) \times 10^{-14}$	298	Langbein et al., 1999	PLP-UVA
Relative Rate Coefficients			
$<3 \times 10^{-13}$	300 ± 3	McLoughlin et al., 1993	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-CHF_2OCF_2CHFCl-diethyl ether air mixtures at ~1 bar pressure. The concentrations of CHF_2OCF_2CHFCl and diethyl ether were measured by GC. The measured upper limit to the rate coefficient ratio k(HO + CHF_2OCF_2CHFCl)/k(HO + diethyl ether) is placed on an absolute basis by using a rate coefficient of k(HO + diethyl ether) = 1.31×10^{-11} cm^3 molecule^{-1} s^{-1} at 300 K (Atkinson, 1994).

Preferred Values

$k = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.5 \times 10^{-13}$ exp(-1230/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250-430 K.

Reliability

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

Comments on Preferred Values

The study of Tokuhashi et al. (1999) used samples of CHF_2OCF_2CHFCl purified by GC (99.999% purity as analyzed by GC), and the 298 K rate coefficients obtained using three independent techniques (PLP-LIF, FP-LIF and DF-LIF) were identical within the experimental errors. The earlier measurements of Brown et al. (1989; 1990) at 302 K and 422 K are higher than the data of Tokuhashi et al. (1999), probably in part because of the presence of reactive impurities in the CHF_2OCF_2CHFCl sample used by Brown et al. (1989; 1990) [see Tokuhashi et al. (1999)]. The 298 K rate coefficients from the absolute rate studies of Tokuhashi et al. (1999) and Langbein et al. (1999) are in excellent agreement, and the preferred values are based on these two studies. The upper limit to the rate coefficient measured by McLoughlin et al. (1993) is consistent with the preferred values.

References

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IV.A2.147

$$\mathbf{HO_2 + CF_3CCl_2O_2 \rightarrow O_2 + CF_3CCl_2O_2H}$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.9 \pm 0.7) \times 10^{-12}$	298	Hayman et al., 1994	LP-UVA (a)

Comments

(a) Laser flash photolysis-UV absorption study of CF_3CCl_3-CH_3OH-O_2-N_2 mixtures. The kinetic data were obtained by analyzing two sets of transient decays for $CF_3CCl_2O_2$ and HO_2 radicals on the basis of a mechanism consisting of 10 reactions.

Preferred Values

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

Reliability

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

Comments on Preferred Values

While the above value of the rate coefficient seems reasonable, it has been derived from the analysis of a complex chemical system and requires independent verification to reduce the recommended error limits. It is interesting to note, by comparison with data for analogous halogenated RO_2 radicals, that while the α-substitution of Cl appears to reduce the rate coefficient slightly, the presence of the CF_3 group causes a much larger reduction in the value of k.

References

Hayman, G. D., Jenkin, M. E., Murrells, T. P. and Johnson, C. E.: Atmos. Environ. 28A, 421, 1994.

IV.A2.148

$$\mathbf{HO_2 + CH_2ClO_2} \rightarrow \mathbf{CH_2ClO_2H + O_2} \quad (1)$$
$$\rightarrow \mathbf{HC(O)Cl + H_2O + O_2} \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$3.26 \times 10^{-13} \exp[(822 \pm 63)/T]$	251-600	Catoire et al., 1994	FP-UVA (a)
$(4.9 \pm 0.6) \times 10^{-12}$	298		
Branching Ratios			
$k_1/k = 0.27 \pm 0.05$	295	Wallington et al., 1996	UVP-FTIR (b)
$k_2/k = 0.73 \pm 0.12$			

Comments

(a) Flash photolysis-UV absorption study of Cl_2-CH_3Cl-CH_3OH-O_2-N_2 mixtures at a total pressure of 1013 mbar. Kinetic data were obtained by analyzing pairs of decay curves recorded at two monitoring wavelengths, with differing contributions to the total absorption made by CH_2ClO_2 and HO_2 radicals.

(b) Steady-state photolysis of Cl_2-CH_3Cl-H_2-O_2-N_2 mixtures at total pressures of 933 mbar with FTIR spectroscopic monitoring of the removal of CH_3Cl and formation of CH_2ClO_2H and HCOCl as a function of the initial concentration ratio $[H_2]/[CH_3Cl]$.

Preferred Values

$k = 5.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.2 \times 10^{-13} \exp(820/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-600 K.
$k_1/k = 0.3$
$k_2/k = 0.7$

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 300$ K.
$\Delta (k_1/k) = \pm 0.1$ at 298 K.
$\Delta (k_2/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred branching ratios are based on the results of the product study of Wallington et al. (1996), which demonstrate the participation of both reaction channels, with channel (2) dominating at 298 K. This is fully consistent with previous studies of the oxidation of CH_3Cl (Sanhueza and Heicklen, 1975; Niki et al., 1980), in which near-quantitative formation of HCOCl was observed, even though CH_2ClO_2 was believed to be partially removed by reaction with HO_2. Tentative observation of CH_2ClO_2H at yields up to ca. 10% in these earlier studies is also consistent with the branching ratios reported by Wallington et al. (1996).

The preferred rate coefficient values are based on the sole kinetics study of Catoire et al. (1994). These results indicate that the rate coefficients of the reactions of CH_2ClO_2 and CH_3O_2 radicals with the HO_2 radical at 298 K are similar, as are their temperature dependences. This is in marked contrast to the self reactions of CH_2ClO_2 and CH_3O_2 radicals where chlorine substitution greatly enhances the rate coefficient. Confirmation of the above data is required.

References

Catoire, V., Lesclaux, R., Lightfoot, P. D. and Rayez, M.-T.: J. Phys. Chem. 98, 2889, 1994.
Niki, H., Maker, P. D., Savage, C. M. and Breitenbach, L. P.: Int. J. Chem. Kinet. 12, 1001, 1980.
Sanhueza, E. and Heicklen, J.: J. Phys. Chem. 79, 7, 1975.
Wallington, T. J., Hurley, M.D. and Schneider, W.F.: Chem. Phys. Lett. 251, 164, 1996.

IV.A2.149

$$\begin{aligned} \mathbf{HO_2 + CHCl_2O_2} &\rightarrow \mathbf{CHCl_2O_2H + O_2} && \mathbf{(1)} \\ &\rightarrow \mathbf{C(O)Cl_2 + H_2O + O_2} && \mathbf{(2)} \\ &\rightarrow \mathbf{HC(O)Cl + HOCl + O_2} && \mathbf{(3)} \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.6 \times 10^{-13} \exp[(700 \pm 64)/T]$	286-440	Catoire et al., 1996	FP-UVA (a)
$(5.46 \pm 0.77) \times 10^{-12}$	300		
Branching Ratios			
$k_2/k = 0.71$	295	Catoire et al., 1996	UVP-FTIR (b)
$k_3/k = 0.29$			

Comments

(a) Flash photolysis of $CHCl_3$ in the presence of CH_3OH-O_2-N_2 mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from $CHCl_2O_2$ and HO_2) were recorded in the wavelength range 220 nm to 250 nm. k derived in conjunction with optimization of the rate coefficient for the self-reaction of $CHCl_2O_2$, using a five reaction mechanism.

(b) Steady-state photolysis of Cl_2 or F_2 in the presence of CH_2Cl_2-H_2-O_2-N_2 mixtures at a total pressure of 933 mbar with FTIR spectroscopic monitoring of the removal of CH_2Cl_2 and formation of HCOCl and $COCl_2$ as a function of the initial concentration ratio $[H_2]/[CH_2Cl_2]$.

Preferred Values

$k = 5.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.6 \times 10^{-13} \exp(700/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280-440 K.
$k_2/k = 0.7$ at 298 K.
$k_3/k = 0.3$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 300$ K.
$\Delta (k_1/k) = \pm 0.2$ at 298 K.
$\Delta (k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred branching ratios are based on the results of the product study of Catoire et al. (1996), which provide evidence for the participation of reaction channels (2) and (3), through observation of $C(O)Cl_2$ and HC(O)Cl formation, respectively. No evidence for formation of the hydroperoxide, $CHCl_2OOH$, by channel (1) was obtained. The existence of an alternative channel forming O_2, OH and $CHCl_2O$ (and therefore HC(O)Cl from $CHCl_2O$ decomposition) could not be ruled out on the basis of the product studies alone; but no evidence for a radical-forming channel was apparent from the kinetics measurements in the same study.

The preferred rate coefficient values are based on the sole kinetics study of Catoire et al. (1996). These results indicate that the rate coefficients of the reactions of CH_3O_2, CH_2ClO_2, $CHCl_2O_2$ and CCl_3O_2 radicals with the HO_2 radical at 298 K are similar, as are their temperature dependences. This is in marked contrast to the self-reactions, for which chlorine substitution greatly enhances the rate coefficient. Confirmation of the above sole determination is required.

References

Catoire, V., Lesclaux, R., Schneider, W. F. and Wallington, T. J.: J. Phys. Chem. 100, 14356, 1996.

IV.A2.150

$$\begin{aligned} \mathbf{HO_2 + CF_2ClO_2} &\rightarrow \mathbf{O_2 + CF_2ClO_2H} \quad &\mathbf{(1)} \\ &\rightarrow \mathbf{O_2 + COF_2 + HOCl} \quad &\mathbf{(2)} \\ &\rightarrow \mathbf{O_2 + FCOCl + HOF} \quad &\mathbf{(3)} \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.4 \pm 1.7) \times 10^{-12}$	296	Hayman and Battin-Leclerc, 1995	LP-UVA (a)

Comments

(a) Flash photolysis of H_2O_2 in the presence of CHF_2Cl-O_2-N_2 mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from CF_2ClO_2 and HO_2) were recorded in the wavelength range 220 nm to 240 nm. k derived from simulations of the decay traces using a 10 reaction mechanism.

Preferred Values

$k = 3.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

While the above value of the rate coefficient seems reasonable, it has been derived from the analysis of a complex chemical system and requires independent verification to reduce the recommended error limits.

The rate coefficients for the reactions of HO_2 with a number of halogenated peroxy radicals suggest that the presence of an α-F atom has a deactivating influence. Consistent with this, k is apparently somewhat lower than those for the corresponding reactions of CH_3O_2, CH_2ClO_2, $CHCl_2O_2$ and CCl_3O_2, which all lie in the range (5-6) × 10^{-12} cm^3 molecule^{-1} s^{-1}.

References

Hayman, G. and Battin-Leclerc, F.: J. Chem. Soc. Faraday Trans. 91, 1313, 1995.

IV.A2.151

$$\mathbf{HO_2 + CCl_3O_2} \begin{array}{ll} \rightarrow \mathbf{CCl_3O_2H + O_2} & \mathbf{(1)} \\ \rightarrow \mathbf{C(O)Cl_2 + HOCl + O_2} & \mathbf{(2)} \end{array}$$

Rate coefficient data (k = k_1 + k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.8 \times 10^{-13} \exp[(706 \pm 31)/T]$	298-374	Catoire et al., 1996	FP-UVA (a)
$(4.9 \pm 0.6) \times 10^{-12}$	300		
Branching Ratios			
k_2/k = 1.0	295	Catoire et al., 1996	UVP-FTIR (b)

Comments

(a) Flash photolysis of CCl_4 in the presence of CH_3OH-O_2-N_2 mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from CCl_3O_2 and HO_2) were recorded in the wavelength range 220 nm to 250 nm. k derived from simulations of the decay traces using a six reaction mechanism.

(b) Steady-state photolysis of Cl_2 or F_2 in the presence of $CHCl_3$-H_2-O_2-N_2 mixtures at a total pressure of 933 mbar with FTIR spectroscopic monitoring of the removal of $CHCl_3$ and formation of $C(O)Cl_2$ as a function of the initial concentration ratio $[H_2]/[CH_2Cl_2]$. $C(O)Cl_2$ was the only carbon-containing product observed, with a yield of 100% (within experimental error) under all conditions.

Preferred Values

$k = 5.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.7 \times 10^{-13} \exp(710/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280-440 K.
k_2/k = 1.0 at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 300$ K.
$\Delta (k_2/k) = ^{+0.0}_{-0.1}$ at 298 K.

Comments on Preferred Values

The results of the product study of Catoire et al. (1996) are consistent with the reaction proceeding exclusively via channel (2). The preferred rate coefficient values are based on the results of the same study, which is the only study of this reaction. These results indicate that the rate coefficients of the reactions of CH_3O_2, CH_2ClO_2, $CHCl_2O_2$ and CCl_3O_2 radicals with the HO_2 radical at 298 K are similar, as are their temperature dependences. This is in marked contrast to the self-reactions, for which chlorine substitution greatly enhances the rate coefficient. Confirmation of the above sole determination is required.

References

Catoire, V., Lesclaux, R., Schneider, W. F. and Wallington, T. J.: J. Phys. Chem. 100, 14356, 1996.

IV.A2.152

$$\mathbf{HO_2 + CFCl_2CH_2O_2 \rightarrow O_2 + CFCl_2CH_2O_2H \quad (1)}$$
$$\mathbf{\rightarrow O_2 + CFCl_2CHO + H_2O \quad (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.2 \pm 4.6) \times 10^{-12}$	296	Hayman and Battin-Leclerc, 1995	LP-UVA (a)

Comments

(a) Flash photolysis of H_2O_2 in the presence of $CFCl_2CH_3$-O_2-N_2 mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from $CFCl_2CH_2O_2$ and HO_2) were recorded in the wavelength range 220 nm to 240 nm. k derived from simulations of the decay traces using a 10 reaction mechanism.

Preferred Values

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

Reliability

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

Comments on Preferred Values

While the above value of the rate coefficient seems reasonable, it has been derived from the analysis of a complex chemical system and requires independent verification to reduce the recommended error limits. Within the uncertainty of the determination, k is indistinguishable from that recommended for the reaction of HO_2 with $C_2H_5O_2$, suggesting that the presence of the $CFCl_2$ group has only a minor influence on the reaction.

References

Hayman, G. and Battin-Leclerc, F.: J. Chem. Soc. Faraday Trans. 91, 1313, 1995.

IV.A2.153

$$\mathbf{HO_2 + CF_2ClCH_2O_2 \rightarrow O_2 + CF_2ClCH_2O_2H} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow O_2 + CF_2ClCHO + H_2O} \quad \mathbf{(2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.8 \pm 3.4) \times 10^{-12}$	296	Hayman and Battin-Leclerc, 1995	LP-UVA (a)

Comments

(a) Flash photolysis of H_2O_2 in the presence of CF_2ClCH_3-O_2-N_2 mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from $CF_2ClCH_2O_2$ and HO_2) were recorded in the wavelength range 220 nm to 240 nm. k derived from simulations of the decay traces using a 10 reaction mechanism.

Preferred Values

$k = 6.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

While the above value of the rate coefficient seems reasonable, it has been derived from the analysis of a complex chemical system and requires independent verification to reduce the recommended error limits. Within the uncertainty of the determination, k is indistinguishable from that recommended for the reaction of HO_2 with $C_2H_5O_2$, suggesting that the presence of the CF_2Cl group has only a minor influence on the reaction.

References

Hayman, G. and Battin-Leclerc, F.: J. Chem. Soc. Faraday Trans. 91, 1313, 1995.

IV.A2.154

$NO_3 + C_2HCl_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.0 \times 10^{-13} \exp(-2030/T)$	278-368	Noremsaune et al., 1997	DF-Vis (a)
$(4.43 \pm 0.32) \times 10^{-16}$	295		
Relative Rate Coefficients			
$(2.9 \pm 0.2) \times 10^{-16}$	298	Atkinson et al., 1987	RR (b)
$(3.8 \pm 0.4) \times 10^{-16}$	298	Noremsaune et al., 1997	RR (c)
$(4.7 \pm 1.1) \times 10^{-16}$	298	Noremsaune et al., 1997	RR (d)
$(3.6 \pm 0.9) \times 10^{-16}$	298	Chew et al., 1998	RR (e)

Comments

(a) NO_3 was generated by F + HNO_3 and detected by optical absorption in a multi-pass cell. Experiments conducted under pseudo-first order conditions.

(b) The relative decay rates of C_2HCl_3 and C_2H_4 were monitored in N_2O_5-NO_2-organic-air mixtures at one atmosphere total pressure of air to obtain: $k(NO_3 + C_2HCl_3)/k(NO_3 + C_2H_4) = (1.37 \pm 0.08)$. This rate coefficient ratio was placed on an absolute basis using $k(NO_3 + C_2H_4) = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) NO_3 was formed in the thermal decomposition of N_2O_5 in mixtures containing C_2HCl_3 and ethene as reference reactant at total pressures of 1013 mbar N_2. The addition of ethane as a Cl atom scavenger had no effect. $k(NO_3 + C_2HCl_3)/k(NO_3 + C_2H_4)$ was measured to be (1.79 ± 0.18). This was placed on an absolute basis using $k(NO_3 + C_2H_4) = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(d) NO_3 was formed in the thermal decomposition of N_2O_5 in mixtures containing C_2HCl_3 and C_2H_3Cl as reference reactant at total pressures of 1013 mbar N_2. Addition of ethane as a Cl atom scavenger had no effect. $k(NO_3 + C_2HCl_3)/k(NO_3 + C_2H_3Cl)$ was measured to be (1.3 ± 0.04). This was placed on an absolute basis using $k(NO_3 + C_2H_3Cl) = (3.7 \pm 0.8) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (Noremsaune et al., 1997).

(e) NO_3 was formed in the thermal decomposition of N_2O_5 in mixtures containing C_2HCl_3 and 2,3-dimethylbutane as reference reactant at total pressures of 990 mbar air. Depletion of reactants was monitored by GC-FID. Addition of ethane as Cl and OH atom scavenger. $k(NO_3 + C_2HCl_3)/k(NO_3$ + 2,3-dimethylbutane) was measured to be (0.82 ± 0.21). This was placed on an absolute basis using $k(NO_3$ + 2,3-dimethylbutane) $= 4.39 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k = 3.5 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.2 \times 10^{-13} \exp(-2030/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270-370 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred value is derived from the relative rate coefficients measured by Atkinson et al. (1987) and Noremsaune et al. (1997) determined relative to ethene, and Chew et al. (1998) relative to 2,3-dimethybutane. The temperature dependence is based on the result of Noremsaune et al. (1997), the only measurement over a range of temperatures. Their A-factor has been modified to reproduce the recommended rate constant at 298 K. There are several product channels open, resulting in formation of trichloroepoxyethane, dichloracetylchloride, chloroformyl and carbonylchloride (Noremsaune et al., 1995; Perez-Casany et al., 2000).

References

Atkinson, R., Aschmann, S. M. and Goodman, M. A.: Int. J. Chem. Kinet., 19, 299, 1987.
Chew, A. A., Atkinson, R. and Aschmann, S. M.: J. Chem. Soc. Faraday Trans., 94, 1083, 1998.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Noremsaune, I. M. W., Hjorth, J. and Nielsen, C. J.: J. Atmos. Chem., 21, 223, 1995.
Noremsaune, I. M. W., Langer, S., Ljungström, E. and Nielsen, C. J.: J. Chem. Soc., Faraday Trans. 93, 525, 1997.
Perez-Casany, M. P., Nebot-Gil, I. and Sanchez-Martin, J.: J. Phys. Chem. A, 104, 11340, 2000.

IV.A2.155

$NO_3 + C_2Cl_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.6 \pm 8.1) \times 10^{-17}$	295	Noremsaune et al., 1997	DF-Vis (a)
Relative Rate Coefficients			
$<5 \times 10^{-17}$	298	Atkinson et al., 1987	RR (b)
$(8 \pm 3) \times 10^{-17}$	299	Noremsaune et al., 1997	RR (c)
4×10^{-17}	299	Noremsaune et al., 1997	RR (d)
$<1.8 \times 10^{-16}$	298	Chew et al., 1998	RR (e)

Comments

(a) NO_3 generated by F + HNO_3 and detected by optical absorption in a multi-pass cell. Experiments conducted under pseudo-first order conditions.

(b) Derived by monitoring the relative decay rates of C_2Cl_4 and C_2H_4 in N_2O_5-NO_2-organic-air mixtures at one atmosphere total pressure of air. The observations yielded $k(NO_3 + C_2Cl_4)/k(NO_3 + C_2H_4) = < 0.25$. This upper limit to the rate coefficient ratio was placed on an absolute basis by use of $k(NO_3 + C_2H_4) = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) NO_3 formed in the thermal decomposition of N_2O_5 in mixtures containing C_2HCl_3 and ethene as reference reactant at total pressures of 1013 mbar N_2. Addition of ethane as Cl atom scavenger had no effect. $k(NO_3 + C_2Cl_4)/k(NO_3 + C_2H_4)$ was measured to be (0.39 ± 0.11). This was placed on an absolute basis using $k(NO_3 + C_2H_4) = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(d) NO_3 formed in the thermal decomposition of N_2O_5 in mixtures containing C_2Cl_4 and C_2H_3Cl as reference reactant at total pressures of 1013 mbar N_2. Addition of ethane as Cl atom scavenger had no effect. $k(NO_3 + C_2Cl_4)/k(NO_3 + C_2H_3Cl)$ was measured to be 0.1. This was placed on an absolute basis using $k(NO_3 + C_2H_3Cl) = (3.7 \pm 0.8) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (Noremsaune et al. 1997).

(e) NO_3 formed in the thermal decomposition of N_2O_5 in mixtures containing C_2Cl_4 and 2,3-dimethylbutane as reference reactant at total pressures of 990 mbar air. Depletion of reactants was monitored by GC-FID. Addition of ethane as Cl and OH atom scavenger. $k(NO_3 + C_2Cl_4)/k(NO_3 + \text{2,3-dimethylbutane})$ was measured to be (0.21 ± 0.18). This was placed on an absolute basis using $k(NO_3 + \text{2,3-dimethylbutane}) = 4.39 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The preferred value is derived from the relative rate coefficients measured by Atkinson et al. (1987). The upper limit to the rate coefficient has been increased to take into account the spread in the data.

References

Atkinson, R., Aschmann, S. M., and Goodman, M. A.: Int. J. Chem. Kinet., 19, 299, 1987.
Chew, A. A., Atkinson, R. and Aschmann, S. M.: J. Chem. Soc. Faraday Trans., 94, 1083, 1998.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Noremsaune, I. M. W., Langer, S., Ljungström, E. and Nielsen, C. J.: J. Chem. Soc., Faraday Trans. 93, 525, 1997.

IV.A2.156

$$\begin{array}{lll} \mathbf{ClO + CH_3O_2} & \rightarrow \mathbf{ClOO + CH_3O} & \mathbf{(1)} \\ & \rightarrow \mathbf{OClO + CH_3O} & \mathbf{(2)} \\ & \rightarrow \mathbf{HCHO + HCl + O_2} & \mathbf{(3)} \\ & \rightarrow \mathbf{CH_3Cl + O_3} & \mathbf{(4)} \\ & \rightarrow \mathbf{CH_3OCl + O_2} & \mathbf{(5)} \end{array}$$

$\Delta H^\circ(1) = 4.1$ kJ·mol^{-1}
$\Delta H^\circ(2) = 1.2$ kJ·mol^{-1}
$\Delta H^\circ(3) = -311.5$ kJ·mol^{-1}
$\Delta H^\circ(4) = -49.9$ kJ·mol^{-1}
$\Delta H^\circ(5) = -174.6$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.1 \pm 1.7) \times 10^{-12}$	300	Simon et al., 1989	MM-UVA (a)
$3.25 \times 10^{-12} \exp[-(114 \pm 38)/T]$	225-355	Helleis et al., 1993	DF-MS (b)
2.22×10^{-12}	295		
$(1.9 \pm 0.4) \times 10^{-12}$	293	Kenner et al., 1993	DF-MS (c)
$2.0 \times 10^{-12} \exp[(80 \pm 50)/T]$	233-300	Kukui et al., 1994	DF-MS (d)
$(2.5 \pm 0.3) \times 10^{-12}$	300		
Branching Ratios			
$k_1/k > 0.70$	300	Simon et al., 1989	IR, UV (e)
$k_2/k < 0.05$			
$k_3/k < 0.02$			
$k_1/k = 1.51 \exp[-(218 \pm 93)/T]$	225-295	Helleis et al., 1993	DF-MS (f)
$k_3/k < 0.02$			
$k_5/k = 0.08 \exp[(377 \pm 178)/T]$			
$k_1/k = 0.50 \pm 0.2$	300	Kukui et al., 1994	DF-MS (g)
$k_1/k = 0.63 \pm 0.2$	273		
$k_1/k = 0.38 \pm 0.2$	253		
$k_1/k = 0.26 \pm 0.1$	233		
$k_5/k = 0.011 \exp[(836 \pm 140)/T]$	233-300		
$k_5/k = (T/300)^{-1.65}$ - $0.223 \exp(411/T)$	215-295	Helleis et al., 1994	DF-MS (h)
$k_1/k = 0.21$ - 0.51	298	Biggs et al., 1995	DF-LIF (i)
$k_1/k = 0.3 \pm 0.1$	298	Daële and Poulet, 1996	DF-LIF (j)

Comments

(a) Broad band photolysis of slowly flowing Cl_2-Cl_2O-CH_4-O_2 mixtures at 312 ± 7 mbar. CH_3O_2 and ClO were detected by absorption at 240 nm and 292.2 nm, respectively. The rate constant was derived by fitting time dependent optical density measurements at 240 nm and 292.2 nm to a chemical model.

(b) Flow tube at 2.3-4 mbar He. CH_3O_2 formed in F + CH_4 in the presence of O_2, ClO formed from Cl + Cl_2O, or Cl + OClO or Cl + O_3. Both reactants were monitored at their parent ions by mass spectrometry, and the pseudo first order decay of CH_3O_2 in excess concentration of ClO used to derive k directly.

(c) Flow tube at 2.5 mbar He. CH_3O_2 formed in F + CH_4 in presence of O_2, ClO formed from Cl + O_3. Both reactants were monitored at their parent ions by mass spectrometry, and the pseudo first order decay of CH_3O_2 in excess concentration of ClO used to derive k directly.

(d) Flow tube at 5–6 mbar He. CH_3O_2 formed in F + CH_4 in presence of O_2, ClO formed from Cl + O_3. Both reactants were monitored at their parent ions by mass spectrometry, and the pseudo first order decay of CH_3O_2 in excess concentration of ClO used to derive k directly.

(e) FTIR and UV analysis of flowing gas-mixture (as described in comment (a)). No evidence for OClO formation enabled the upper limit of $k_2/k < 0.05$ to be derived. Also, no evidence for O_3 formation from channel (4). Observed products by FTIR were HCHO, CH_3OH, HCl and HC(O)OH. HC(O)OH profiles were analysed with the assumption that it was formed in reactions of HCHO with HO_2 which allows some differentiation between channels (1) and (3), both of which generate HCHO if O is present, but only one of which generates HO_2. The yield of HC(O)OH was compatible with $k_2/k > 0.7$ and $k_3/k < 0.3$.

(f) (see also comment b). Mass spectrometric detection of products. No evidence was found for formation of OClO, O_3 or CH_3Cl, suggesting that channels 2 and 4 are unimportant. Use of CD_3O_2 enabled sensitive measurement of DCl formation, and an upper limit of 2% for channel 3. HCHO, HOCl and CH_3OCl were positively identified as products. Branching ratios were derived by assuming that CH_3OCl is formed directly in channel (5), whereas HCHO and HOCl arise from channel (1) followed by rapid reaction of CH_3O with ClO, and by calibrating the CH_3O_2 and HCHO signals. The branching ratio to channel (5) was derived by assuming that only channels (1) and (5) are significant (i.e. sum to unity), though the predicted negative temperature dependence of the CH_3OCl yield was observed.

(g) (see also comment d). CH_3O_2 formed in F + CH_4 in presence of O_2, ClO formed from Cl + O_3. No evidence found for formation of OClO or CH_3Cl. Observed products were CH_3OCl, HOCl and HCHO. Branching ratios for CH_3OCl and HCHO derived by quantitative mass spectrometric detection of both CH_3O_2 loss and CH_3OCl or HCHO formation. The parameterisation of the branching ratio k_5/k was derived by fitting to the authors tabulated data. HOCl signals were also converted to temperature dependent values of k_1/k by normalising to $(k_1 + k_5)/k = 1$ at 300 K.

(h) Flow tube at 2.3 mbar He. CH_3O_2 formed in F + CH_4 in presence of O_2, ClO formed from Cl + Cl_2O. Branching ratios derived by quantitative mass spectrometric detection of both CH_3O_2 loss and CH_3OCl formation.

(i) Flow tube at 2.7 mbar He. CH_3O_2 (not detected) formed in F + CH_4 in presence of O_2, ClO (detected by MS) formed from Cl + O_3. CH_3O detected by LIF at 292.8 nm. Derivation of the branching ratio for channel (1) involved modelling CH_3O profiles that were influenced by the presence of CH_3O impurity in the CH_3O_2 source, and reactions of both CH_3O_2 and CH_3O with Cl atoms, and loss of CH_3O by reaction with ClO and at the wall.

(j) Flow tube at 1.3 mbar He. CH_3O_2 formed in F + CH_4 in presence of O_2, ClO (detected by MS) formed from Cl + O_3. CH_3O was detected quantitatively by LIF at 298.3 nm, and CH_3OCl was observed but not quantified. As in comment (i), derivation of the branching ratio required numerical simulation of several processes.

Preferred Values

$k = 2.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.4 \times 10^{-12}$ exp(-20/T) cm^3 molecule^{-1} s^{-1} over the temperature range 220-360 K.

$k_1/k = 0.73$ at 298 K.
$k_1/k = 1.51$ exp(-218/T) from 220 to 300 K.
$k_5/k = 0.15$ at 298 K.
$k_5/k = 0.018$ exp(630/T) from 220 to 300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 200$ K.
$\Delta (k_1/k) = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 150$ K.
$\Delta (k_5/k) = 0.1$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred value of k at 298 K is the unweighted average k from the direct studies of Helleis et al. (1993), Kenner et al. (1993) and Kukui et al. (1994) who all measured the CH_3O_2 radical directly by MS, under pseudo first-order conditions. The recommended value also encompasses the result of Simon et al. (1989), which was obtained indirectly, and is consistent with the upper limit of $k(200\ \text{K}) < 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} set by DeMore (1991). The temperature dependence of k was derived by averaging the values of E/R presented by Helleis et al. (1993) and Kukui et al. (1994) and adjusting the pre-exponential factor to obtain the recommended value of k(298 K).

Although there is consensus that formation of CH_3Cl, O_3, OClO and HCl are insignificant, (Simon et al., 1989; Helleis et al., 1993; Kenner et al., 1993; DeMore, 1991) ruling out channels (2-4), there is disagreement in the branching ratio to channels (1) and (5). The most reliable branching ratio is that to CH_3OCl formation (5), as CH_3OCl is easiest to calibrate, and is a non-reactive product. The preferred branching ratio at 298 K for channel (5) is the averaged result of Helleis et al. (1993) and Kukui et al. (1994). The data of Helleis et al. (1993) are reproduced by the expression: $k_5/k = 0.034 \exp(430/T)$, which was combined with $k_5/k = 0.011 \exp(836/T)$ from Kukui et al. (1994) to obtain the preferred expression for the temperature dependence of branching to channel (5).

There are two direct measurements (Biggs et al., 1995; Daële et al., 1996) of CH_3O formation in channel (1), which required extensive modelling of its further reactions, and which had to take its presence as impurity in the CH_3O_2 source into account (see comments i and j). There are also indirect measurements, which assume rapid conversion of CH_3O to HCHO and HOCl via reaction with the excess ClO, which is borne out in separate studies of the kinetics of this reaction (Daële et al. 1996, Biggs et al. 1995). Helleis et al. (1993) and Kukui et al. (1994) observed formation of both HCHO and HOCl, with kinetics consistent with formation in channel (1) as rate limiting step. Although only HCHO could be accurately calibrated, HOCl signals were consistent with expected ionization efficiencies compared to ClO. The data of Kukui et al. (1994) suffered from a large background under the HCHO peak, which introduced severe uncertainty into their measurement of k_1/k, and the preferred branching ratio for channel 1 at 298 K, and its temperature dependence is therefore taken from Helleis et al. (1993). This data is in excellent agreement with the values of k_1/k which Kukui et al. (1994) derived from HOCl signals and assuming that only channels (1) and (5) contribute at 300 K.

When summed together, channels (1) and (5) are seen to represent 85–90 % of the overall reaction, although these measurements are associated with large errors that do not preclude a significant, so far unconsidered reaction channel, which would potentially also explain the low branching ratios for CH_3O formation obtained. The error limits on k_1/k are expanded to accommodate this. Theoretical work (Drougas et al., 2003) has shown that the reaction proceeds via formation of a CH_3OOOCl association complex on both a singlet surface (decomposing to CH_3O + ClOO, (1)) or a triplet surface (rearranging to form $CH_3OCl + O_2$ (2)), which is consistent with experimental findings.

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IV.A2.157

$$\mathbf{CF_2Cl + O_2 + M \rightarrow CF_2ClO_2 + M}$$

$\Delta H°$ = -127.4 kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.4×10^{-29} $(T/298)^{-5.2}[N_2]$	200-300	Forst and Caralp, 1991	(a)

Comments

(a) Microcanonical variational theory with inversion of partition functions, used for interpolation between experimental data of the reactions O_2 + (CCl_3, CCl_2F and CF_3).

Preferred Values

$k_0 = 1.4 \times 10^{-29}$ $(T/300)^{-5}[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.
$\Delta n = \pm 3$.

Comments on Preferred Values

There are no measurements for this reaction. However, the analysis by Forst and Caralp (1991), as well as a simple interpolation of k_0-values for $CF_3 + O_2$ and $CFCl_2 + O_2$ lead to the given preferred values. Unlike Forst and Caralp (1991), who prefer F_c = 0.6 we recommend F_c= 0.4.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
7.1×10^{-12} $(T/298)^{-0.56}$	200-300	Forst and Caralp, 1991	(a)

Comments

(a) See comment (a) for k_0.

Preferred Values

$k_\infty = 7 \times 10^{-12} (T/298)^{-0.6}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K.

Reliability

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

Comments on Preferred Values

See Comments on Preferred Values for k_0.

References

Forst, W. and Caralp, F.: J. Chem. Soc. Faraday Trans.. 87, 2307, 1991.

IV.A2.158

$CFCl_2 + O_2 + M \rightarrow CFCl_2O_2 + M$

$\Delta H^\circ = -124.6\ kJ \cdot mol^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.0 \pm 0.8) \times 10^{-30}$ [N$_2$]	298	Caralp and Lesclaux, 1983	PP-MS (a)
5.5×10^{-30} $(T/298)^{-6}$[N$_2$]	233-373	Danis, 1991	PLP-MS (b)

Comments

(a) Pulsed laser photolysis-MS study. Falloff curve measure over the range 0.3–16 mbar, extrapolated with F_c= 0.6 and k_∞= 6×10^{-12} cm^3 molecule^{-1} s^{-1}.

(b) As comment (a). Results cited and evaluated by Forst and Caralp (1991).

Preferred Values

$k_0 = 6 \times 10^{-30}$ $(T/298)^{-6}$[N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 230-380 K.

Reliability

$\Delta \log k_0 = \pm\ 0.3$ at 298 K.
$\Delta n = \pm\ 3$.

Comments on Preferred Values

There are only measurements from a single laboratory which were made close to the low pressure limit of the falloff curve. Using F_c values of 0.35–0.4 such as observed for $CCl_3 + O_2$ and $CF_3 + O_2$ would only slightly modify the extrapolated values of k_0 but be of larger influence on k_∞.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6 \pm 1) \times 10^{-12}$	298	Caralp and Lesclaux, 1983	PLP-MS (a)
$(9 \pm 3) \times 10^{-12}$	233-273	Danis, 1991	PLP-MS (b)

Comments

(a) See comment (a) for k_0

(b) See comment (b) for k_0

Preferred Values

$k_\infty = 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

See Comments on Preferred Values for k_0. Using $F_c = 0.4$ instead of 0.6 in the present case would increase k_∞ by a factor of 1.5. The present choice, therefore, is based on the data from Caralp and Lesclaux (1983) and $F_c \approx 0.4$.

References

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IV.A2.159

$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$

ΔH° = -92 kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.8 \pm 0.6) \times 10^{-31}$ [He]	295	Ryan and Plumb, 1984	DF-MS (a)
$(1.6 \pm 0.3) \times 10^{-30} (T/298)^{-6.3}[N_2]$	233-333	Danis et al., 1991	PLP-MS/UVA (b)
$(6.5 \pm 0.2) \times 10^{-31} (T/300)^{-6.1}[N_2]$	298-333	Fenter et al., 1993	PLP-MS/UVA (c)
$(2.7 \pm 0.2) \times 10^{-31} (T/300)^{-8.7}$[He]	286-332	Nottingham et al., 1994	F-MS (d)
$(1.1 \pm 0.3) \times 10^{-30} (T/300)^{-6.3}[N_2]$	260-346	Luther et al., 2001	PLP-UVA (e)
$(4.2 \pm 0.7) \times 10^{-31} (T/298)^{-6.9}$[He]			

Comments

(a) Microwave discharge flow-quadrupole MS study. CCl_3 radicals generated by the reaction F + $CHCl_3 \rightarrow CCl_3$ + HF. Falloff curve studied between 2.3 and 7 mbar of He and extrapolated with $F_c = 0.25$.

(b) Laser photolysis of CCl_4 with MS detection at lower and UV absorption detection at higher pressures. Measurements between 1 and 16 mbar as well as at 930 mbar of N_2. Evaluation with $F_c = \exp(-T/255)$, i.e., $F_c = 0.31$ at 300 K, and $k_\infty = 3.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

(c) Photolysis of CCl_3Br at 248 nm with detection of CCl_3 by MS or UV absorption at 215 nm. Measurements at 1.3–16 mbar (MS detection) and 27–930 mbar (UV absorption detection). Falloff curve represented with $F_c = 0.6$ and $k_\infty = 2.6 \times 10^{-12} \exp(T/300)^{-1.1}$ cm^3 molecule^{-1} s^{-1}.

(d) Flow tube using dissociative electron attachment for radical production and MS for radical detection. Pressures of He below 4 mbar. Measurements evaluated with $F_c = 0.33$ and $k_\infty = 2.74 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 286 K.

(e) Photolysis of CCl_3Br at 248 nm and detection of CCl_3 at 223.5 nm. Measurements at 200, 300, and 346 K over the pressure range 2–900 bar in He and N_2. Data represented with $F_c(N_2) = 0.35 (T/300)^{-0.35}$ and $k_\infty = 5.2 \times 10^{-12} (T/300)^{-1.4}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k_0 = 1.1 \times 10^{-30} (T/300)^{-6.2}[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-350 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are the average of the data from Danis et al. (1991) and Fenter et al. (1993) which are consistent with the falloff extrapolation from Luther et al. (2001). As the experiments were conducted to sufficiently low pressures, the different F_c-values used are of no relevance for the determination of k_0.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
5.1×10^{-12}	300	Cooper et al., 1980	PR-UVA (a)
2.5×10^{-12}	295	Ryan and Plumb, 1984	DF-MS (b)
$(3.2 \pm 0.7) \times 10^{-12}$ $(T/298)^{-1.2}$	233-333	Danis et al., 1991	PLP-MS/UVA (c)
$(2.5 \pm 0.2) \times 10^{-12}$ $(T/298)^{-1.1}$	298-333	Fenter et al., 1993	PLP-MS/UVA (d)
$(5.2 \pm 0.2) \times 10^{-12}$ $(T/300)^{-1.4}$	260-346	Luther et al., 2001	PLP-UVA (e)

Comments

(a) Pulse radiolysis of CCl_4 at 930 mbar of He. CCl_3O_2 radicals detected by UV absorption.

(b) See comment (a) for k_0.

(c) See comment (b) for k_0.

(d) See comment (c) for k_0.

(e) See comment (d) for k_0.

Preferred Values

$k_\infty = 5.2 \times 10^{-12}$ $(T/300)^{-1.4}$ cm^3 molecule^{-1} s^{-1} over the temperature range 260-350 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 1.5$.

Comments on Preferred Values

The combined data by Danis et al. (1991), Fenter et al. (1993) and Luther et al. (2001) at 300 K are well represented by a falloff curve with $F_c = 0.35$. Since the falloff curve has been measured up to very high pressures, the derived values from Luther et al. (2001) for k_∞ are preferred. The small temperature dependence of F_c employed by Luther et al. (2001) may be neglected.

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IV.A2.160-192

$$\mathbf{R_1(R_2)CHO + O_2 \rightarrow R_1COR_2 + HO_2} \quad \mathbf{(1)}$$

$$\mathbf{R_1(R_2)CHO\ (+\ M) \rightarrow products} \quad \mathbf{(2)}$$

R = alkyl, halogenated alkyl, H or halogen atom.

Rate coefficient data

Reaction Number	Reactions		k_1/k_2 cm^3 molecule^{-1}	Temp./K	Reference	Comments
IV.A2.160	$CHFClO + O_2 \rightarrow COFCl + HO_2$	(1)	$k_1[O_2] \ll k_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1993	(a)
IV.A2.161	$CHFClO + M \rightarrow HCOF + Cl + M$	(2)				
IV.A2.162	$CF_2ClO + O_2 \rightarrow$ products	(1)	$k_1[O_2] \ll k_2$ (933 mbar,air)	298	Edney and Driscoll, 1992	(b)
IV.A2.163	$CF_2ClO + M \rightarrow COF_2 + Cl + M$	(2)	$k_2 = 7.0 \times 10^5$	298	Carr et al., 1986;	FP-UVA
			$k_2 = 3 \times 10^{13}\exp(-5250/T)(k/s^{-1})$		Rayez et al., 1987	
IV.A2.164	$CFCl_2O + O_2 \rightarrow$ products	(1)	$k_1[O_2] \ll k_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1993	(c)
IV.A2.165	$CFCl_2O + M \rightarrow COFCl + Cl + M$	(2)	$k_2 = 7.0 \times 10^5$		Lesclaux et al., 1987;	FP-MS
			$k_2 = 3 \times 10^{13}\exp(-5250/T)(k/s^{-1})$		Rayez et al., 1987	
IV.A2.166	$CCl_3O + M \rightarrow COCl_2 + Cl + M$	(2)	$k_2 = 8.0 \times 10^6$		Lesclaux et al., 1987;	FP-MS(c)
			$k_2 = 4 \times 10^{13}\exp(-4600/T)(k/s^{-1})$		Rayez et al., 1987	
IV.A2.167	$CF_2ClCH_2O + O_2 \rightarrow CF_2ClCHO + HO_2$	(1)	$k_1[O_2] \gg k_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1994	(d)
IV.A2.168	$CF_2ClCH_2O + M \rightarrow CF_2Cl + HCHO + M$	(2)				
IV.A2.169	$CFCl_2CH_2O + O_2 \rightarrow CFCl_2CHO + HO_2$	(1)	$k_1[O_2] \gg k_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1994	(e)
IV.A2.170	$CFCl_2CH_2O + M \rightarrow CFCl_2 + HCHO + M$	(2)	$k_1 = 2.0 \times 10^{-15}$	298	Mörs et al., 1996;	(f)
			$k_1 = 1.3 \times 10^{-16}$	298	Wu and Carr, 1996	(g)
			$k_1 = 2.4 \times 10^{-15}\exp[-(944 \pm 55)/T]$	251-341		
IV.A2.171	$CF_3CFClO + O_2 \rightarrow$ products	(1)	$k_1[O_2] \ll k_2$ (933 mbar,air)	298	Edney and Driscoll, 1992	(h)
IV.A2.172	$CF_3CFClO + M \rightarrow CF_3COF + Cl + M$	(2)	$k_1[O_2] \ll k_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1993	(i)
IV.A2.173	$CF_3CCl_2O + O_2 \rightarrow$ products	(1)	$k_1[O_2] \ll k_2$ (933 mbar,air)	298	Edney et al., 1991	(j)
IV.A2.174	$CF_3CCl_2O + M \rightarrow CF_3COCl + Cl + M$	(2)	$k_1[O_2] \ll k_2$ (135 mbar,O_2)	298	Sato and Nakamura, 1991	(k)
			$k_1[O_2] \ll k_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1993	(l)
			$k_1[O_2] \ll k_2$ ($\sim$ 1 bar,air)	298	Hayman et al., 1994	(m)
IV.A2.175	$CF_3CF_2CCl_2O + O_2 \rightarrow$ products	(1)	$k_1[O_2] \ll k_2$ (135 mbar,O_2)	298	Sato and Nakamura, 1991	(n)
IV.A2.176	$CF_3CF_2CCl_2O + M \rightarrow CF_3CF_2COCl + Cl + M$	(2)	$k_1[O_2] \ll k_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1994	(o)
IV.A2.177	$CF_2ClCF_2CFClO + O_2 \rightarrow$ products	(1)	$k_1[O_2] \ll k_2$ (135 mbar,O_2)	298	Sato and Nakamura, 1991	(p)
IV.A2.178	$CF_2ClCF_2CFClO + M \rightarrow CF_2ClCF_2COF + Cl + M$	(2)	$k_1[O_2] \ll k_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1994	(q)
IV.A2.179	$CH_2ClO + O_2 \rightarrow HCOCl + HO_2$	(1)	4.6×10^{-18} (933 mbar, $O_2 + N_2$)	296	Kaiser and Wallington, 1994	(r)
IV.A2.180	$CH_2ClO + M \rightarrow HCO + HCl + M$	(2)	$k_1 = 1.3 \times 10^{-12} \exp[-(934 \pm 128)/T]$	265-306	Wu and Carr, 2001	(s)
			$k_2 = 7.7 \times 10^9 \exp[-(4803 \pm 722)/T]$ (13 mbar)	265-306		
IV.A2.181	$CH_3CHClO + O_2 \rightarrow CH_3COCl + HO_2$	(1)	$k_1[O_2] \ll k_2$ (933 mbar,air)	295	Shi et al., 1993	(t)
IV.A2.182	$CH_3CHClO + M \rightarrow CH_3CO + HCl + M$	(2)	$k_1[O_2] \ll k_2$ (1013 mbar,air)	298	Maricq et al., 1993	(u)
IV.A2.183	$HOCH_2CHClO + O_2 \rightarrow HOCH_2COCl + HCl + HO_2$	(1)	$k_1[O_2] \ll k_2$ (986 mbar,air)	298	Tuazon et al., 1988	(v)
IV.A2.184	$HOCH_2CHClO + M \rightarrow CH_2OH + HCOCl + M$	(2)				
IV.A2.185	$HOCHClCH_2O + O_2 \rightarrow HOCHClCHO + HO_2$	(1)	$k_1[O_2] \ll k_2$ (986 mbar,air)	298	Tuazon et al., 1988	(v)
IV.A2.186	$HOCHClCH_2O + M \rightarrow CHClOH + HCHO + M$	(2)				
IV.A2.187	$CH_3CCl_2O + O_2 \rightarrow$ products	(1)	$k_1[O_2] \ll k_2$ (933 mbar, O_2)	298	Nelson et al., 1990	(w)
IV.A2.188	$CH_3CCl_2O + M \rightarrow CH_3COCl + Cl + M$	(2)				
IV.A2.189	$CCl_3CH_2O + O_2 \rightarrow CCl_3CHO + HO_2$	(1)	$k_1[O_2] \ll k_2$ (933 mbar, O_2)	298	Nelson et al., 1990	(x)
IV.A2.190	$CCl_3CH_2O + M \rightarrow CCl_3 + HCHO + M$	(2)				
IV.A2.191	$CCl_3CCl_2O + O_2 \rightarrow$ products	(1)	$k_1[O_2] \ll k_2$	298	Sato and Nakamura, 1991	(y)
IV.A2.192	$CCl_3CCl_2O + M \rightarrow CCl_3COCl + Cl + M$	(2)				

Comments

(a) Steady-state photolysis of Cl_2 in the presence of CH_2FCl-air mixtures (986 mbar) with FTIR absorption spectroscopic analyses: a 100% yield of HCOF was observed, consistent with $k_1[O_2] \ll k_2$.

(b) Steady-state photolysis of Cl_2 in the presence of CHF_2Cl-air mixtures (933 mbar) with FTIR absorption spectroscopic analysis: a 111 ± 6% yield of COF_2 was observed, consistent with $k_1[O_2] \ll k_2$, The cited absolute values for k_2 were derived from evaluation of data of Carr et al. (1986) and Rayez et al. (1987) reported in IUPAC Supplement IV, 1992.

(c) Similar experiments to those of Comment (a) at a total pressure of 986 mbar, but with $CHFCl_2$ a 100% yield of COF_2 was observed, consistent with $k_1[O_2] \ll k_2$. The cited absolute values for k_2 were derived from evaluation of data of Lesclaux et al. (1987) and Rayez et al. (1987) reported in IUPAC Supplement IV, 1992.

(d) Steady-state photolysis of Cl_2 in the presence of CH_3CF_2Cl-air mixtures (986 mbar) with FTIR absorption spectroscopic analyses: an ∼ 100% yield of CF_2ClCHO was observed, consistent with $k_1[O_2] \gg k_2$.

(e) Steady-state photolysis of Cl_2 in the presence of CH_3CFCl_2-air mixtures (986 mbar) with FTIR absorption spectroscopic analysis: an ∼ 100% yield of $CFCl_2CHO$ was observed, consistent with $k_1[O_2] \gg k_2$. Experiments on this reaction were also carried out by Edney and Driscoll (1992) and Tuazon and Atkinson (1993).

(f) Direct time-resolved experiment using laser pulsed photolysis-laser long path absorption; $CFCl_2CH_2O$ produced by $CFCl_2CH_2O_2$ + NO reaction.

(g) UV flash photolysis of $CFCl_2CH_3/N_2/O_2$ mixtures (13–50 mbar); growth and decay of $CFCl_2CH_2O$ radicals in excess O_2 measured by time resolved MS.

(h) Steady-state photolysis of Cl_2 in the presence of CF_3CHFCl-air mixtures (1 atm) with FTIR absorption spectroscopic analyses: a 100 ± 4% yield of $CF_3C(O)F$ was observed, consistent with $k_1[O_2] \ll k_2$.

(i) Steady-state photolysis of Cl_2 in the presence of CF_3CHFCl-air mixtures at 986 mbar total pressure with FTIR absorption spectroscopic analyses: a 101 ± 1% yield of $CF_3C(O)F$ was observed, consistent with $k_1[O_2] \ll k_2$.

(j) Steady-state photolysis of Cl_2 in the presence of CF_3CHCl_2-air mixtures (933 mbar) with FTIR absorption spectroscopic analyses: a ∼ 100% yield of $CF_3C(O)Cl$ was observed, consistent with $k_1[O_2] \ll k_2$.

(k) Similar experiments to those of Comment (j) at a total pressure of 133 mbar. The observed formation of $CF_3C(O)Cl$ is consistent with $k_1[O_2] \ll k_2$.

(l) Similar experiments to those of Comment (i) at a total pressure of 986 mbar, but with CF_3CHCl_2: a 98% yield of $CF_3C(O)Cl$ was observed, consistent with $k_1[O_2] \ll k_2$.

(m) Steady-state photolysis of Cl_2 in the presence of CF_3CHCl_2-air mixtures (∼ 1 atm) with broad-band UV absorption analyses: a ∼ 100% yield of $CF_3C(O)Cl$ was observed, consistent with $k_1[O_2] \ll k_2$.

(n) Similar experiments to those of Comment (k) at a total pressure of 133 mbar. The observed formation of $CF_3CF_2C(O)Cl$ is consistent with $k_1[O_2] \ll k_2$.

(o) Steady-state photolysis of Cl_2 in the presence of $CF_3CF_2CHCl_2$-air mixtures at 986 mbar with FTIR spectroscopic analyses: a 100% yield of $CF_3CF_2C(O)Cl$ was observed, consistent with $k_1[O_2] \ll k_2$.

(p) Steady-state photolysis of Cl_2 in the presence of $CHFClCF_2CF_2Cl$-O_2 mixtures (133 mbar) with FTIR spectroscopic analyses: observed formation of $CF_2ClCF_2C(O)F$ is consistent with $k_1[O_2] \ll k_2$.

(q) Steady-state photolysis of Cl_2 in the presence of CF_2ClCF_2CHFCl-air mixtures (986 mbar) with FTIR spectroscopic analysis: a 99% yield of $CF_2ClCF_2C(O)F$ was observed, consistent with $k_1[O_2] \ll k_2$.

(r) Steady-state photolysis of Cl_2 in the presence of CH_3Cl-O_2-N_2 mixtures with FTIR absorption spectroscopic analysis of HC(O)Cl, CO, HCl and CH_2ClOOH products. k_1/k_2 based on yields of CO and HC(O)Cl, the latter being corrected for secondary formation and removal. The ratio k_1/k_2 was found to be markedly pressure dependent over the range 12 to 933 mbar, and the cited value refers to 700 Torr (933 mbar) total pressure.

(s) UV flash photolysis - time resolved MS. Pressure = 7–50 mbar; growth of HCOCl and HCl products used to determine kinetics.

(t) Steady-state photolysis of Cl_2 in the presence of C_2H_5Cl-O_2-N_2 mixture with FTIR spectroscopic analysis of products: the observed high yields of HCl (157%) and CO_2 (53%) were explained by reaction (2).

(u) Laser flash photolysis of Cl_2 in the presence of C_2H_5Cl-air mixtures with infrared absorption detection of HCl. The observed secondary formation of HCl was explained by reaction (2).

(v) Steady-state photolysis of CH_3ONO or C_2H_5ONO in the presence of chloroethene -NO-air mixtures, with and without C_2H_6 as an added Cl atom scavenger. FTIR spectroscopic analysis of HCHO and HCOCl products, with close to unit yields of each. These products and their formation yields are consistent with the qualitative relative values of $k_1[O_2]$ and k_2 shown above.

(w) Steady-state photolysis of CH_3CCl_3-O_2 mixtures in the presence of Br_2 or NO (to scavenge Cl atoms), with GC and IR analyses of products. CH_3COCl was the major product observed, consistent with the relative values of $k_1[O_2]$ and k_2 shown above.

(x) Steady-state photolysis of Cl_2 in the presence of CH_3CCl_3-O_2 mixtures with GC and IR analyses of CCl_3CHO and $COCl_2$, which are consistent with the relative values of $k_1[O_2]$ and k_2 shown above.

(y) Steady-state photolysis of Cl_2 in the presence of $CHCl_2CCl_3$-O_2 mixtures (133 mbar) with FTIR spectroscopic analysis. The observed formation yields of CCl_3COCl and $COCl_2$ are consistent with $k_1[O_2] \ll k_2$.

Preferred Values

$R_1(R_2)CHO = CH_2ClO$

$k_1/k_2 = 4.6 \times 10^{-18}$ cm^3 molecule^{-1} at 298 K.

Comments on Preferred Values

$R_1(R_2)CHO = CH_2ClO, CH_3CHClO$

The elimination of HCl occurs from the CH_3CHClO radical (Shi et al., 1993, Maricq et al., 1993) as well as from the CH_2ClO radical (Kaiser and Wallington, 1994; Wu and Carr, 2001).

$R_1(R_2)CHO$ = other radicals in the above table.

For the purpose of atmospheric modeling studies it is recommended that the above qualitative information on the ratios k_1/k_2 be used to decide if one or other of the alkoxy radical reaction pathways predominates or if both pathways should be considered.

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IV.A2.193-202

$$\begin{array}{lll} \mathbf{RO_2 + NO} & \mathbf{\rightarrow RO + NO_2} & \mathbf{(1)} \\ \mathbf{RO_2 + NO + M} & \mathbf{\rightarrow RONO_2 + M} & \mathbf{(2)} \end{array}$$

(R= CH_2Cl, CHFCl, CF_2Cl, $CFCl_2$, CCl_3, CH_3CFCl, CF_2ClCH_2, $CFCl_2CH_2$, CF_3CCl_2,CH_2ClCH_2)

Rate coefficient data (k = k_1 + k_2)

Reaction Number	k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients				
IV.A2.193	R=CH_2Cl			
	$(1.87 \pm 0.20) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
IV.A2.194	R = CHFCl			
	$(1.31 \pm 0.20) \times 10^{-11}$	299	Bhatnagar and Carr, 1996	FP-MS (b)
IV.A2.195	R=CF_2Cl			
	$1.6 \times 10^{-11} (T/298)^{-(1.5\pm0.4)}$	230-430	Dognon et al., 1985	PLP-MS (c)
	$(1.6 \pm 0.3) \times 10^{-11}$	298		
	$(1.31 \pm 0.12) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
IV.A2.196	R=$CFCl_2$			
	$(1.6 \pm 0.2) \times 10^{-11}$	298	Lesclaux and Caralp, 1984	PLP-MS (d)
	$1.45 \times 10^{-11} (T/298)^{-(1.3\pm0.2)}$	230-430	Dognon et al., 1985	PLP-MS (c)
	$(1.45 \pm 0.2) \times 10^{-11}$	298		
IV.A2.197	R=CCl_3			
	$(1.86 \pm 0.28) \times 10^{-11}$	295	Ryan and Plumb, 1984	DF-MS (e)
	$1.7 \times 10^{-11} (T/298)^{-(1.0\pm0.2)}$	230-430	Dognon et al., 1985	PLP-MS (c)
	$(1.7 \pm 0.2) \times 10^{-11}$	298		
IV.A2.198	R=CH_3CFCl			
	$2.0 \times 10^{-11} (T/300)^{-(1.8\pm0.3)}$	263-321	Wu and Carr, 1996	FP-MS (f)
	1.9×10^{-11}	298		
IV.A2.199	R=CF_2ClCH_2			
	$(1.18 \pm 0.10) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
IV.A2.200	R=$CFCl_2CH_2$			
	$(1.28 \pm 0.11) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
	$1.3 \times 10^{-11} (T/300)^{-(1.5\pm0.2)}$	263-321	Wu and Carr, 1996	FP-MS (f)
	1.25×10^{-11}	298		
IV.A2.201	R=CF_3CCl_2			
	$(1.5–2.0) \times 10^{-11}$	298	Hayman et al., 1994	PLP-AS (g)
IV.A2.202	R=CH_2ClCH_2			
	$(9.7 \pm 1.2) \times 10^{-12}$	298	Patchen et al., 2005	DF-CIMS (h)

Comments

(a) k determined from $+d[NO_2]/dt$ at a total pressure of 1 bar.

(b) Photolysis of Cl_2 in the presence of CH_2FCl, O_2, N_2 and NO at 8–33 mbar total pressure. k was obtained from the formation kinetics of NO_2. k was independent of pressure in the studied range.

(c) No significant pressure dependence in k over the range 1.3–13 mbar was observed.

(d) Measurements were made at 2.7 mbar total pressure.

(e) k independent of pressure over the range 2.3–7.2 mbar.

(f) Photolysis of CH_3CFCl_2 in the presence of O_2, N_2 and NO at 11–27 mbar total pressure. k for both CH_3CFClO_2 and $CFCl_2CH_2O_2$ were extracted simultaneously from the removal kinetics of NO and formation kinetics of $CFCl_2CH_2O$. k was independent of pressure in the studied range.

(g) k derived from computer fit of transient absorption traces based on a mechanism of 9 reactions. Experiments performed at 1 bar pressure.

(h) $CH_2ClCH_2O_2$ generated from the C_2H_4 + Cl reaction, with k determined from pseudo-first order decay $CH_2ClCH_2O_2$ in the presence of NO. Measurements made at 130 mbar pressure.

Preferred Values

R = CH_2Cl
$k = 1.9 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$\Delta \log k = \pm 0.3$ at 298 K.

R = CHFCl
$k = 1.3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$\Delta \log k = \pm 0.3$ at 298 K.

R = CF_2Cl
$k = 1.5 \times 10^{-11} (T/298)^{-1.5}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 230-430 K.
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta n = \pm 0.5$.

R = $CFCl_2$
$k = 1.5 \times 10^{-11} (T/298)^{-1.3}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 230-430 K.
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta n = \pm 0.5$.

R = CCl_3
$k = 1.8 \times 10^{-11} (T/298)^{-1.0}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 230-430 K.
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta n = \pm 0.5$.

R = CH_3CFCl
$k = 2.0 \times 10^{-11} (T/298)^{-1.8}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 260-320 K.
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$.

R = CF_2ClCH_2
$k = 1.2 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$\Delta \log k = \pm 0.3$ at 298 K.

R = $CFCl_2CH_2$
$k = 1.3 \times 10^{-11} (T/298)^{-1.5}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 260-320 K.
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta n = \pm 0.5$.

R = CF_3CCl_2
$k = 1.8 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$\Delta \log k = \pm 0.3$ at 298 K.

R = CH_2ClCH_2
$k = 9.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

R = CF_2ClCH_2, CH_2Cl
The preferred values are the rounded-off rate coefficients determined by Sehested et al. (1993).

R = CHFCl
The preferred value is the rounded-off rate coefficient determined by Bhatnagar and Carr (1996).

R = CF_2Cl
The preferred values are based on the temperature dependent data of Dognon et al. (1985), adjusted to fit the average value of k_{298} from the data of Sehested et al.(1993) and Dognon et al. (1985).

R = $CFCl_2$
The preferred values are based on the temperature dependent data of Dognon et al. (1985), adjusted to fit the average value of k_{298} from the data of Lesclaux and Caralp (1984), and Dognon et al. (1985).

R = CH_3CFCl
The preferred values are based on the temperature dependent data of Wu and Carr (1996).

R = $CFCl_2CH_2$
The preferred value is the rounded-off average of the rate coefficients determined by Sehested et al. (1993) and Wu and Carr (1996).

R = CF_3CCl_2
The preferred value is the mid-point of the range of values determined by Hayman et al. (1994).

R = CH_2ClCH_2
The preferred value is the rate coefficient determined by Patchen et al. (2005).

R = CCl_3 The preferred values are based on the temperature dependent data of Dognon et al. (1985), adjusted to fit the average value of k_{298} from the data of Ryan and Plumb (1984) and Dognon et al. (1985).

The temperature dependence expressions are given in the form favoured by Dognon et al. (1985), and subsequently adopted by others, which best describe the measured data. Comparison of the reported rate coefficients with those for the corresponding alkyl peroxy radicals, CH_3O_2 and $C_2H_5O_2$, indicates that the presence of a α-halogen substituent typically enhances k_{298} by a factor of about 1.5–2, with the reactions also possessing a similar dependence on temperature where comparison is possible. Although not so marked, it appears that additional α-halogen substituents result in further slight enhancements to k_{298}. Similarly to small alkyl peroxy radicals, the observations indicate that the reactions are dominated by the RO-forming channel (1). Dognon et al. (1985) measured quantum yields for NO_2 greater than unity for all the RO_2 radicals studied; suggesting that the RO_2 + NO reactions mainly form RO and NO_2, with additional NO_2 being produced from secondary chemistry. Nishida et al. (2004) have observed formation of a small yield $1.7 \pm 0.3\%$ of CF_3ONO_2 from the reaction of CF_3O_2 with NO, confirming the existence of channel (2) at 930 mbar pressure. This suggests that the reactions of the C_1 and C_2 halogenated RO_2 radicals will generally have minor channels forming $RONO_2$, but additional studies are required to confirm this.

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IV.A2.203

$$\mathbf{CF_2ClO_2 + NO_2 + M \rightarrow CF_2ClO_2NO_2 + M}$$

$\Delta H° = -107$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.8 \pm 1.8) \times 10^{-29}$ [O_2]	298	Moore and Carr, 1990	FP-MS (a)
$(5.0 \pm 1.0) \times 10^{-29}$ $(T/298)^{-6.2}$[O_2]	248-324	Wu and Carr, 1991	FP-MS (b)

Comments

(a) CF_2ClO_2 radicals generated by flash photolysis of CF_2ClBr in the presence of O_2 and detected by MS. Measurements over the pressure range 1.3–13 mbar, extrapolated with $F_c = 0.6$ and $k_\infty = 5.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

(b) As comment (a). $F_c = 0.78 \exp(-T/569)$, i. e., F_c (298) = 0.46, and $k_\infty = 4.5 \times 10^{-12}$ $(T/298)^{-2.5}$ cm^3 molecule^{-1} s^{-1} used for extrapolation.

Preferred Values

$k_0 = 5 \times 10^{-29}$ $(T/298)^{-6.2}$[N_2] cm^3 molecule^{-1} s^{-1}cm^3 over the temperature range 250–320 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 2$.

Comments on Preferred Values

The pressure dependence in the investigated pressure range fits well to that observed at higher pressures for the reverse dissociation by Köppenkastrop and Zabel (1991) and the theoretical modellings by Destriau and Troe (1990) and by Caralp et al. (1988). Uncertainties of the used $F_c = 0.46$ at 298 K do not much influence the values of the derived k_0. Therefore the values from Wu and Carr (1991) are our preferred values, assuming equal values of k_0 for the bath gases O_2 and N_2.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
5.2×10^{-12}	298	Moore and Carr, 1990	(a)
4.5×10^{-12} $(T/298)^{-2.5}$	248-324	Wu and Carr, 1991	(b)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0. The measurements were performed so far from the high pressure range that extrapolations were uncertain.

Preferred Values

$k_\infty = 6.3 \times 10^{-12} (T/298)^{-0.7}$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-320 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The unusually large negative temperature coefficient of k_∞ derived by Wu and Carr (1991) signals problems with the falloff extrapolations. For this reason it appears safer to employ the falloff curves for $CF_2ClO_2NO_2$ dissociation from Köppenkastrop and Zabel (1991), which were studied over a ten times larger pressure range extending up to higher pressures. Doing this, the preferred value is derived which is consistent with our preferred data for $CF_3O_2 + NO_2$. As for the reverse reaction, F_c= 0.30 is recommended.

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IV.A2.204

$$CF_2ClO_2NO_2 + M \rightarrow CF_2ClO_2 + NO_2 + M$$

ΔH° = 107 kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.8 \times 10^{-3} \exp(-10500/T)$ [N_2]	273–288	Köppenkastrop and Zabel, 1991	(a)
$1.1 \times 10^{-3} \exp(-10762/T)$ [N_2]	276-289	Xiong and Carr, 1994	(b)

Comments

(a) Thermal decomposition of $CF_2ClO_2NO_2$ in a temperature-controlled (± 0.1°C) 420 liter reaction chamber. The reactant was monitored in situ by long-path IR absorption. N_2 pressures of 11, 82, and 800 mbar were employed. Falloff extrapolations with F_c= 0.30 and $k_\infty = 1.6 \times 10^{16} \exp(-11990/T)$ s^{-1}.

(b) Continuous-flow temperature-controlled (± 1°C) photoreactor coupled to MS. N_2 pressures of 4–53 mbar were employed. Falloff extrapolations made with F_c = 0.45 and $k_\infty = 6.7 \times 10^{16} \exp(-11871/T)$ s^{-1}.

Preferred Values

$k_0 = 1.8 \times 10^{-3} \exp(-10500/T)$ [N_2] s^{-1} over the temperature range 270–290 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The measurements of Köppenkastrop and Zabel (1991) and of Xiong and Carr (1994) differ markedly in their pressure dependences which is reflected by large differences of the extrapolated k_∞. As the pressure dependence observed by Xiong and Carr (1994) is much larger than given by theoretical falloff curves from Destriau and Troe (1990) and Caralp et al. (1988), the measurements by Xiong and Carr (1994) have to be in error for some unknown reason and are not considered here. Instead, the results from Köppenkastrop and Zabel (1991), which were obtained over a ten times larger pressure range, here are preferred with F_c = 0.30 and k_∞ such as given below.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.6 \times 10^{16} \exp(-11990/T)$	273-288	Köppenkastrop and Zabel, 1991	(a)
$6.7 \times 10^{16} \exp(-11871/T)$	276-289	Xiong and Carr, 1994	(b)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0. The given value for k_∞ actually stems from a combination of recombination data, equilibrium constants and theoretical modelling. It is consistent with the observed pressure dependence.

Preferred Values

k_∞ = 1.6 × 10^{16} exp(-11990/T) s^{-1} over the temperature range 270-290 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

See Comments on Preferred Values of k_0.

References

Caralp, F., Lesclaux, R., Rayez, M.-T., Rayez, J.-C. and Forst, W.: J. Chem. Soc. Faraday Trans. 2, 84, 569, 1988.
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IV.A2.205

$$\mathbf{CFCl_2O_2 + NO_2 + M \rightarrow CFCl_2O_2NO_2 + M}$$

ΔH° = -107 kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.5) \times 10^{-29}$ [O_2]	298	Lesclaux and Caralp, 1984	PLP-MS (a)
$(3.5 \pm 0.5) \times 10^{-29}$ $(T/298)^{-4.1}$ [O_2]	233-373	Lesclaux et al., 1986	PLP-MS (b)
$(5.5 \pm 1.6) \times 10^{-29}$ $(T/298)^{-5.5}$ [O_2]	233-373	Caralp et al., 1988	PLP-MS (c)

Comments

(a) Pulsed laser photolysis with MS detection of $CFCl_2O_2$. Pressure range 1.3–13 mbar. Falloff extrapolation with F_c = 0.6 and $k_\infty = 6.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(b) As comment (a). Falloff extrapolation with F_c = 0.6 and $k_\infty = 5.9 \times 10^{-12}$ $(T/298)^{-0.72}$ cm^3 molecule^{-1} s^{-1}.

(c) As comment (a). Falloff extrapolation using F_c = exp($-T$/342), i.e. F_c = 0.42 at 298 K, and $k_\infty = 8.3 \times 10^{-12}$ $(T/298)^{-0.66}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k_0 = 5.5 \times 10^{-29}$ $(T/298)^{-5.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 230–380 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 2$.

Comments on Preferred Values

The data from Caralp et al. (1988) are preferred because they employ a value of F_c = 0.42. However, this value should be used independent of the temperature. Equal values of k_0 for the bath gases O_2 and N_2 are assumed.

High-pressure rate coefficients

Rate coefficient data

k_∞/ cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.0 \pm 1.0) \times 10^{-12}$	298	Lesclaux and Caralp, 1984	(a)
$(5.9 \pm 1.0) \times 10^{-12}$ $(T/298)^{-0.72}$	233-373	Lesclaux et al., 1986	(b)
$(8.3 \pm 1.0) \times 10^{-12}$ $(T/298)^{-0.66}$	233-373	Caralp et al., 1988	(c)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

(c) See comment (c) for k_0.

Preferred Values

$k_\infty = 8.3 \times 10^{-12} (T/298)^{-0.66}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-380 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

See Comments on Preferred Values for k_0.

References

Caralp, F., Lesclaux, R., Rayez, M.-T., Rayez, J.-C. and Forst, W.: J. Chem. Soc. Faraday Trans. 2, 84, 569, 1988.
Lesclaux, R. and Caralp, F.: Int. J. Chem. Kinet., 16, 1117, 1984.
Lesclaux, R., Caralp, F. and Dognon, A. M.: Geophys. Res. Lett., 13, 933, 1986.

IV.A2.206

$$CFCl_2O_2NO_2 + M \rightarrow CFCl_2O_2 + NO_2 + M$$

$\Delta H^\circ = 107$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.0 \times 10^{-2} \exp(-10860/T)$ [N_2]	260-300	Köppenkastrop and Zabel, 1991	(a)

Comments

(a) Reaction studied in a temperature-controlled 420 liter reaction chamber, monitoring the reactant by long-path IR absorption. Measurements at 11, 82, and 800 mbar pressure. Falloff extrapolations using $F_c = 0.28$ and $k_\infty = 6.6 \times 10^{16} \exp(-12240/T)$ s^{-1}.

Preferred Values

$k_0 = 1.0 \times 10^{-2} \exp(-10860/T)$ [N_2] s^{-1} over the temperature range 260–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The only available measurements are preferred with the employed $F_c = 0.28$. The data are consistent with related reactions.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.0 \times 10^{16} \exp(-12300/T)$	274-305	Simonaitis et al., 1979	(a)
$6.0 \times 10^{16} \exp(-12240/T)$	260-300	Köppenkastrop and Zabel, 1991	(b)

Comments

(a) Steady-state photolysis of Cl_2-$CHFCl_2$-O_2-NO-NO_2 mixtures at 1 bar. Simulation of the mechanism depending on the extent of various Cl-consuming reactions. k was assumed to be close to k_∞.

(b) See comment (a) for k_0.

Preferred Values

k_∞ = 6.6 × 10^{16} exp(-12240/T) s^{-1} over the temperature range 260-300 K.

Reliability

Δ log k_∞ = ± 0.3 at 298 K.
Δ (E/R) = ± 500 K.

Comments on Preferred Values

The agreement between the results from Simonatis et al. (1979) and Köppenkastrop and Zabel (1991) at 298 K and 1 bar within a factor of 1.5 appears satisfactory. The data from Köppenkastrop and Zabel (1991) are preferred.

References

Köppenkastrop, D. and Zabel, F.: Int. J. Chem. Kinet., 23, 1, 1991.
Simonaitis, R., Glavas, S. and Heicklen, J.: Geophys. Res. Lett., 6, 385, 1979.

IV.A2.207

$CCl_3O_2 + NO_2 + M \rightarrow CCl_3O_2NO_2 + M$

ΔH° = -105.6 kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/ cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.2 \pm 3) \times 10^{-29}$ $(T/298)^{-6.0}$ [O_2]	233-373	Caralp et al., 1988	PLP-MS (a)

Comments

(a) Pulsed laser photolysis-MS study at pressures of 1.3–13 mbar. Falloff extrapolation with F_c = exp(-T/260), i.e. F_c = 0.32 at 298 K and $k_\infty = 1.49 \times 10^{-12}$ $(T/298)^{-0.3}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k_0 = 9.2 \times 10^{-29}$ $(T/298)^{-6.0}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 230–380 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 2$.

Comments on Preferred Values

There is a single experimental study only. However, according to the analysis by Destriau and Troe (1990) it falls in line with related reactions. Equal values for k_0 are assumed for the bath gases O_2 and N_2. The F_c value should be used independent of the temperature.

High-pressure rate coefficients

Rate coefficient data

k_∞/ cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.49 \pm 0.8) \times 10^{-12}$ $(T/298)^{-0.3}$	233-373	Caralp et al., 1988	PLP-MS (a)

Comments

(a) See comment (a) for k_0.

Preferred Values

$k_\infty = 1.5 \times 10^{-12}$ $(T/298)^{-0.7}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-380 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$

Comments on Preferred Values

See Comments on Preferred Values for k_0. Recommending a temperature-independent $F_c = 0.32$ is consistent with changing n from -0.3 to -0.7 such as preferred for related reactions.

References

Caralp, F., Lesclaux, R., Rayez, M.-T., Rayez, J.-C. and Forst, W.: J. Chem. Soc. Faraday Trans. 2, 84, 569, 1988.
Destriau, M. and Troe, J.: Int. J. Chem. Kinet., 22, 915, 1990.

IV.A2.208

$CCl_3O_2NO_2 + M \rightarrow CCl_3O_2 + NO_2 + M$

ΔH° = 105.6 kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
6.3×10^{-3} exp(-10235/T) [N_2]	260-300	Köppenkastrop and Zabel, 1991	(a)

Comments

(a) Thermal decomposition of $CCl_3O_2NO_2$ studied in a temperature-controlled 410 liter reaction chamber. The reactant was monitored by in situ long-path IR absorption. Pressures of N_2 of 11, 82, and 800 mbar were employed. The data were extrapolated with F_c = 0.22 and k_∞ = 4.8×10^{16} exp(-11820/T) s^{-1}.

Preferred Values

k_0 = 4.3×10^{-3} exp(-10235/T) [N_2] s^{-1} over the temperature range 260–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

There is a single study of the falloff curve only. However, it is consistent with data for the reverse reaction from Caralp et al. (1988). Some readjustment will be necessary to make F_c identical for the forward and reverse reaction, for which F_c = 0.32 was chosen. If F_c = 0.32 replaces F_c = 0.22, k_0 for the dissociation decreases by about a factor of 0.7 such as preferred here.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.42×10^{16} exp(-11500/T)	274-305	Simonaitis et al., 1979	(a)
0.24	298		
6.6×10^{16} exp(-12240/T)	260-300	Köppenkastrop and Zabel, 1991	(b)
0.29	298		

Comments

(a) Steady-state photolysis of Cl_2-$CHCl_3$-O_2-N_2-NO-NO_2 mixtures at 1 bar. Product formation monitored by IR spectroscopy. Some assumption about the mechanism had to be made. The reaction was assumed to be at the high pressure limit.

(b) See comment (a) for k_0.

Preferred Values

k_∞ = 4.8 × 10^{16} exp(-11820/T) s^{-1} over the temperature range 260-300 K.

Reliability

Δ log k_∞ = ± 0.3 at 298 K.
Δ (E/R) = ± 500 K.

Comments on Preferred Values

The two available measurements are in close agreement such that k_∞ appears well established. For the falloff curve see Comments on Preferred Values for k_0.

References

Köppenkastrop, D. and Zabel, F.: Int. J. Chem. Kinet., 23, 1, 1991.
Simonaitis, R., Glavas, S. and Heicklen, J.: Geophys. Res. Lett., 6, 385, 1979.

IV.A2.209

$$\mathbf{C_2H_5O_2 + CF_3CCl_2O_2 \rightarrow CH_3CHO + CF_3CCl_2OH + O_2 \quad (1)}$$
$$\mathbf{\rightarrow C_2H_5O + CF_3CCl_2O + O_2 \quad (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_1 = (3.6 \pm 0.5) \times 10^{-12}$	298	Hayman et al., 1994	PLP-UVA (a)
$k_2 = (9^{+9}_{-5}) \times 10^{-13}$	298		

Comments

(a) Laser flash photolysis-UV absorption study of CF_3CCl_3-C_2H_6-O_2-N_2 mixtures. Kinetic data were obtained by analyzing two sets of transient decays on the basis of a mechanism consisting of 13 reactions.

Preferred Values

$k_1 = 3.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

While the above values of the rate coefficients appear reasonable, they have been derived from the analysis of a complex chemical system and require independent verification to reduce the recommended error limits.

References

Hayman, G. D., Jenkin, M. E., Murrells, T. P. and Johnson, C. E.: Atmos. Environ., 28A, 421, 1994.

IV.A2.210

$$\mathbf{CF_2ClCH_2O_2 + CF_2ClCH_2O_2 \rightarrow CF_2ClCH_2OH + CF_2ClCHO + O_2 \quad (1)}$$
$$\mathbf{\rightarrow CF_2ClCH_2O + CF_2ClCH_2O + O_2 \quad (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_{obs} = (4.13 \pm 0.58) \times 10^{-12}$	298	Wallington and Nielsen, 1991	FP-UVA (a,b)
Branching Ratios			
$k_2/k \approx 1.0$	298	Tuazon and Atkinson, 1994	UV-P-FTIR (c)

Comments

(a) k_{obs} is based on the measured overall second-order decay of $CF_2ClCH_2O_2$, defined by -d[$CF_2ClCH_2O_2$]/dt = $2k_{obs}$ [$CF_2ClCH_2O_2$]^2. As described in detail by Lesclaux (1997), HO_2 radicals formed from the subsequent chemistry of CF_2ClCH_2O (formed from channel (2)) are expected to lead to secondary removal of $CF_2ClCH_2O_2$. The true value of k is expected to fall in the range $k_{obs}/(1+\alpha) < k < k_{obs}$ where $\alpha = k_2/k$.

(b) Pulse radiolysis study of CF_2ClCH_3-O_2-SF_6 mixtures over the pressure range 150–1000 mbar. $CF_2ClCH_2O_2$ radicals were monitored by UV absorption with $\sigma_{250\ nm} = (3.38 \pm 0.68) \times 10^{-18}$ cm^2 molecule^{-1} .

(c) Photolysis of Cl_2 in the presence of CF_2ClCH_3-air mixtures at 987 mbar pressure. In situ monitoring of reactants and products by FTIR spectroscopy was consistent with formation of CF_2ClCHO with a yield ca. 100%, once corrections were made for secondary removal.

Preferred Values

$k_1 = 2.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 1.0$ at 298 K.

Reliability

$\Delta \log k_1 = \pm 0.4$ at 298 K.
$\Delta (k_2/k) = ^{+0.0}_{-0.2}$ at 298 K.

Comments on Preferred Values

The observed formation of CF_2ClCHO in ca. 100% yield from CF_2ClCH_3 oxidation in the product study of Tuazon and Atkinson (1994) is consistent with the reaction proceeding predominantly via the radical forming channel (2), followed by reaction of CF_2ClCH_2O with O_2 to form CF_2ClCHO and HO_2. This also indicates that secondary removal of $CF_2ClCH_2O_2$ by reaction with HO_2 must generate CF_2ClCHO as the major carbon-containing product, in a similar fashion to the observed dominant formation of HC(O)Cl from the reaction of HO_2 with CH_2ClO_2 (Wallington et al., 1996).

The preferred value of k at 298 K is derived from the k_{obs} value reported by Wallington and Nielsen (1991). Similar to a procedure adopted by Lesclaux (1997) for peroxy radicals for which the self reaction rate coefficients are $\geq$ ca. 2×10^{-12} cm^3 molecule^{-1} s^{-1}, k is estimated to be $k_{obs}/(1 + 0.5(k_2/k))$, with this approximation assuming that the secondary reaction of HO_2 with $CF_2ClCH_2O_2$ competes equally with its removal via $HO_2 + HO_2$. The reliability range reflects that k has been derived by this approximate procedure. Confirmatory kinetics and product studies are required.

References

Lesclaux, R.: Combination of peroxyl radicals in the gas phase. In 'Peroxyl Radicals', edited by Alfassi, Z. B.. John Wiley and Sons, 1997.
Tuazon, E. C. and Atkinson, R.: Environ. Sci. Technol., 28, 2306, 1994.
Wallington, T. J. and Nielsen, O. J.: Int. J. Chem. Kinet., 23, 785, 1991.
Wallington, T. J., Hurley, M. D. and Schneider, W. F.: Chem. Phys. Lett., 251, 164, 1996.

IV.A2.211

$$\begin{aligned} \mathbf{CFCl_2CH_2O_2 + CFCl_2CH_2O_2} &\rightarrow \mathbf{CFCl_2CH_2OH + CFCl_2CHO + O_2} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{CFCl_2CH_2O + CFCl_2CH_2O + O_2} \quad \mathbf{(2)} \end{aligned}$$

Rate coefficient data (k= k_1 + k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
k_{obs} = (4.36 ± 0.64) × 10^{-12}	298	Wallington and Nielsen, 1991	PR-UVA (a,b)
Branching Ratios			
$k_2/k \approx 1.0$	298	Tuazon and Atkinson, 1994	UV-P-FTIR (c)

Comments

(a) k_{obs} is based on the measured overall second-order decay of $CFCl_2CH_2O_2$, defined by -d[$CFCl_2CH_2O_2$]/dt = 2k_{obs} [$CFCl_2CH_2O_2$]^2. As described in detail by Lesclaux (1997), HO_2 radicals formed from the subsequent chemistry of $CFCl_2CH_2O$ (formed from channel (2)) are expected to lead to secondary removal of $CFCl_2CH_2O_2$. The true value of k is expected to fall in the range $k_{obs}/(1+\alpha) < k < k_{obs}$ where $\alpha = k_2/k$.

(b) Pulse radiolysis study of $CFCl_2CH_3$-O_2-SF_6 mixtures over the pressure range 152–1013 mbar. $CFCl_2CH_2O_2$ radicals were monitored by UV absorption with $\sigma_{250\ nm}$ = (3.38 ± 0.68) × 10^{-18} cm^2 molecule^{-1} .

(c) Photolysis of Cl_2 in the presence of $CFCl_2CH_3$-air mixtures at 987 mbar pressure. In situ monitoring of reactants and products by FTIR spectroscopy was consistent with formation of $CFCl_2CHO$ with a yield ca. 100%, once corrections were made for secondary removal.

Preferred Values

k_1 = 2.9 × 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.
k_2/k = 1.0 at 298 K.

Reliability

$\Delta \log k_1 = \pm 0.4$ at 298 K.
$\Delta (k_2/k) = ^{+0.0}_{-0.2}$ at 298 K.

Comments on Preferred Values

The observed formation of $CFCl_2CHO$ in ca. 100% yield from $CFCl_2CH_3$ oxidation in the product study of Tuazon and Atkinson (1994) is consistent with the reaction proceeding predominantly via the radical forming channel (2), followed by reaction of $CFCl_2CH_2O$ with O_2 to form $CFCl_2CHO$ and HO_2. This also indicates that secondary removal of $CFCl_2CH_2O_2$ by reaction with HO_2 must generate $CFCl_2CHO$ as the major carbon-containing product, in a similar fashion to the observed dominant formation of HCOCl from the reaction of HO_2 with CH_2ClO_2 (Wallington et al., 1996).

The preferred value of k at 298 K is derived from the k_{obs} value reported by Wallington and Nielsen (1991). Similar to a procedure adopted by Lesclaux (1997) for peroxy radicals for which the self reaction rate coefficients are ≥ ca. 2 × 10^{-12} cm^3 molecule^{-1} s^{-1}, k is estimated to be $k_{obs}/(1 + 0.5(k_2/k))$, with this approximation assuming that the secondary reaction of HO_2 with $CFCl_2CH_2O_2$ competes equally with its removal via HO_2 + HO_2. The reliability range reflects that k has been derived by this approximate procedure. Confirmatory kinetics and product studies are required.

References

Lesclaux, R.: Combination of peroxyl radicals in the gas phase. In ’Peroxyl Radicals’, edited by Alfassi, Z. B., John Wiley and Sons, 1997.
Tuazon, E. C. and Atkinson, R.: Environ. Sci. Technol., 28, 2306, 1994.
Wallington, T. J. and Nielsen, O. J.: Int. J. Chem. Kinet., 23, 785, 1991.
Wallington, T. J., Hurley, M. D. and Schneider, W. F.: Chem. Phys. Lett., 251, 164, 1996.

IV.A2.212

$CF_3CCl_2O_2 + CF_3CCl_2O_2 \rightarrow CF_3CCl_2O + CF_3CCl_2O + O_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_{obs} = (3.33 \pm 0.53) \times 10^{-12}$	295	Wallington et al., 1994	PR-UVA (a,b)
$(3.6 \pm 0.5) \times 10^{-12}$	298	Hayman et al., 1994	LP-UVA (c)

Comments

(a) k_{obs} is based on the measured overall second-order decay of $CF_3CCl_2O_2$, defined by $-d[CF_3CCl_2O_2]/dt = 2k_{obs}[CF_3CCl_2O_2]^2$.

(b) Pulse radiolysis study of CF_3CHCl_2-O_2-SF_6 mixtures over the pressure range of 1013 mbar. $CF_3CCl_2O_2$ radicals were monitored by UV absorption with $\sigma_{250\,nm} = (1.70 \pm 0.26) \times 10^{-18}$ cm^2 molecule^{-1}. The derived value of k was determined from the measured overall second-order decay of $CF_3CCl_2O_2$ radicals.

(c) $CF_3CCl_2O_2$ radicals were generated by 193 nm laser flash photolysis of CF_3CCl_3-CH_3OH-O_2-N_2 mixtures and CF_3CCl_3-C_2H_6-O_2-N_2 mixtures at a total pressure of 1013 mbar. $CF_3CCl_2O_2$ radicals were monitored by UV absorption in the range 230–270nm, with $\sigma_{250\,nm} = (1.79 \pm 0.18) \times 10^{-18}$ cm^3 molecule^{-1}. k determined from global simulation of two sets of transient decays observed at 230, 240, 250, 260 and 270 nm using a 15 reaction mechanism. Rate coefficients for the reactions $CF_3CCl_2O_2$ with HO_2 and $C_2H_5O_2$ were determined simultaneously.

Preferred Values

$k = 3.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The reported formation of $CF_3C(O)Cl$ with approximately 100% yield from CF_3CHCl_2 oxidation in a number of product studies (Edney et al., 1991; Tuazon and Atkinson, 1993; Hayman et al., 1994) has established that the self-reaction of $CF_3CCl_2O_2$ proceeds essentially exclusively via formation of CF_3CCl_2O radicals, which decompose by elimination of Cl. This is also supported by the UV spectral study of $CF_3CCl_2O_2$ by Jemi-Alade et al. (1991), involving flash photolysis-UV absorption of Cl_2 in the presence of CF_3CHCl_2 and O_2. In that study, no decay in the absorption due to $CF_2CCl_2O_2$ was observed over a 40 ms time scale, demonstrating near-quantitative regeneration of Cl atoms, and therefore $CF_3CCl_2O_2$, in the system.

The kinetics studies of Wallington et al. (1994) and Hayman et al. (1994) reported UV absorption spectra for $CF_3CCl_2O_2$ which are in excellent agreement in both shape and magnitude with that reported by Jemi-Alade et al. (1991). The values of k reported by Wallington et al. (1994) and Hayman et al. (1994) are also in close agreement, even though only the methodology of Hayman et al. (1994) was designed to preclude the regeneration of $CF_3CCl_2O_2$, and to extract the true value of k. It is noted that Wallington et al. (1994) made use of concentrations of $CF_3CCl_2O_2$ radicals which were an order of magnitude higher than those in the experiments of Hayman et al. (1994) (and Jemi-Alade et al. (1991)), such that other secondary reactions of CF_3CCl_2O and/or Cl might partially preclude regeneration of $CF_3CCl_2O_2$, or lead to secondary removal of $CF_3CCl_2O_2$. The agreement with the study of Hayman et al. (1994) is therefore likely to be fortuitous. The preferred value at 298 K is based on the rate coefficient reported by Hayman et al. (1994), with the reliability range reflecting the requirement to simulate a comparatively complex system to extract k. Further kinetics studies are required to allow k to be defined more accurately.

References

Edney, E. O., Gay, Jr., B. W. and Driscoll, D. J.: J. Atmos. Chem., 12, 105, 1991.
Hayman, G. D., Jenkin, M. E., Murrells, T. P. and Johnson, C. E.: Atmos. Environ., 28A, 421, 1994.
Jemi-Alade, A. A., Lightfoot, P. D. and Lesclaux, R.: Chem. Phys. Lett., 179, 119, 1991.
Tuazon, E. C. and Atkinson, R.: J. Atmos. Chem., 17, 179, 1993.
Wallington, T. J., Ellermann, T. and Nielsen, O. J.: Res. Chem. Intermed., 20, 265, 1994.

IV.A2.213

$$\mathbf{CH_2ClO_2 + CH_2ClO_2 \rightarrow CH_2ClOH + HC(O)Cl + O_2 \quad (1)}$$
$$\mathbf{\rightarrow 2CH_2ClO + O_2 \quad (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_{obs} = 3.1 \times 10^{-13} \exp[(735 \pm 95)/T]$	228-380	Dagaut et al., 1988	FP-UVA (a,b)
$k_{obs} = (3.78 \pm 0.45) \times 10^{-12}$	289		
$1.95 \times 10^{-13} \exp[(874 \pm 26)/T]$	251-600	Catoire et al., 1994	FP-UVA (c)
$(4.2 \pm 0.4) \times 10^{-12}$	298		
$(3.3 \pm 0.7) \times 10^{-12}$	298	Biggs et al., 1999	DF-LIF/RF (d)
Branching Ratios			
$k_2/k \approx 1.0$	305	Sanhueza and Heicklen, 1975	UVP-IR (e)
$k_2/k \approx 1.0$	298	Niki et al., 1980	UVP-FTIR (f)

Comments

(a) k_{obs} is based on the measured overall second-order decay of CH_2ClO_2, defined by -d[CH_2ClO_2]/dt = $2k_{obs}[CH_2ClO_2]^2$. As described in detail by Lesclaux (1997), HO_2 radicals formed from the subsequent chemistry of CH_2ClO (formed from channel (2)) are expected to lead to secondary removal of CH_2ClO_2. The true value of k is expected to fall in the range $k_{obs}/(1 + \alpha) < k < k_{obs}$, where $\alpha = k_2/k$.

(b) Flash photolysis of Cl_2 in the presence of CH_3Cl-O_2-N_2 mixtures at total pressures of 33–533 mbar at 298 K and of 133 mbar (N_2) from 228–380 K. Peroxy radical concentrations were monitored by UV absorption with $\sigma_{250\ nm} = (3.14 \pm 0.45) \times 10^{-18}$ cm^2 molecule^{-1}.

(c) Flash photolysis of Cl_2 in the presence of CH_3Cl-O_2-N_2 mixtures at a total pressure of 1000 mbar. Peroxy radical concentrations were monitored by UV absorption in the wavelength range 205 to 290 nm, with $\sigma_{250\ nm} = (3.40 \pm 0.20) \times 10^{-18}$ cm^2 molecule^{-1} in the temperature range 251 to 393 K (decreasing at higher temperatures). Values of $k_{obs}/\sigma_{250\ nm}$ are in excellent agreement with those of Dagaut et al. (1988) over the common temperature range. Observed decays in transient absorption were found to be distorted from second order kinetics at wavelengths < 250 nm where HO_2 absorbs significantly, allowing k and the rate coefficient for the reaction of HO_2 with CH_2ClO_2 to be extracted via an iterative procedure.

(d) Experiments performed at pressures in the range 1.3 to 4 mbar. CH_2ClO_2 radicals were produced by the F + CH_3Cl reaction, with subsequent addition of O_2. CH_2ClO_2 radicals were monitored by titration to NO_2 following reaction with excess NO, with LIF detection of NO_2. HO_2 radicals generated from the subsequent chemistry of CH_2ClO (formed from channel (2)) were also titrated to NO_2 under the experimental conditions, but were independently measured through detection of simultaneously formed HO, by RF. k values were extracted by numerical simulation of the results, using an 8 reaction scheme.

(e) Photolysis of Cl_2 in the presence of CH_3Cl-O_2 mixtures. In situ monitoring of products by IR showed exclusive formation of HCl and HC(O)Cl as the initial products.

(f) Photolysis of Cl_2 in the presence of CH_3Cl-air mixtures. In situ monitoring of reactants and products by FTIR spectroscopy showed 90-95% conversion of CH_3Cl to HC(O)Cl. Tentative observation of CH_2ClOOH at yields up to ca. 10%, and H_2O_2, is indicative of the occurrence of partial reaction of HO_2 with CH_2ClO_2 in competition with the HO_2 self reaction.

Preferred Values

$k = 3.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.9 \times 10^{-13} \exp(870/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-600 K.
$k_2/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 200$ K.
$\Delta (k_2/k) = ^{+0.0}_{-0.1}$ at 298 K.

Comments on Preferred Values

The results of the product studies (Sanhueza and Heicklen, 1975; Niki et al., 1980) are consistent with the radical-forming channel (2) being essentially exclusive for the self-reaction of CH_2ClO_2 radicals.

The preferred value of k at 298 K is the average of the results of Catoire et al. (1994) (based on their Arrhenius expression) and Biggs et al. (1999), which allowed extraction of k from full appraisal of the reaction mechanism. The preferred Arrhenius expression for k is based on the E/R value from the comprehensive temperature dependence study of Catoire et al. (1994), combined with a pre-exponential factor adjusted to give the preferred value of k at 298 K. As noted above, the earlier k_{obs} data of Dagaut et al. (1988) are also in excellent agreement with those of Catoire et al. (1994) when both sets of data are analyzed by a simple second-order treatment from results derived at λ= 250 nm, and are therefore also consistent with this recommendation.

References

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IV.A2.214

$$\begin{aligned} \mathbf{CHCl_2O_2 + CHCl_2O_2} &\rightarrow \mathbf{CHCl_2OH + C(O)Cl_2 + O_2} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{CHCl_2O + CHCl_2O + O_2} \quad \mathbf{(2)} \end{aligned}$$

Rate coefficient data (k = k_1 + k_2)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
(1-10) × 10^{-12}	300	Catoire et al., 1996	FP-UVA (a)
(7.0 ± 1.8) × 10^{-12}	298	Biggs et al., 1999	DF-LIF (b)
Branching Ratios			
$k_2/k \geq 0.85$	305	Sanhueza and Heicklen, 1975	UVP-IR (c)
$k_2/k \geq 0.88$	298	Niki et al., 1980	UVP-FTIR (d)
$k_2/k \geq 0.85$	298	Catoire et al., 1996	UVP-FTIR (e)
$k_2/k \geq 0.9$	250-325	Catoire et al., 1996	FP-UVA (f)

Comments

(a) Flash photolysis of $CHCl_3$ in the presence of CH_3OH-O_2-N_2 mixtures at a total pressure of 1000 mbar. Decays in transient absorption signals (with contributions from $CHCl_2O_2$ and HO_2) were recorded in the wavelength range 220 nm to 250 nm. Approximate value of k derived in conjunction with determination of the rate coefficient for the reaction of $CHCl_2O_2$ with HO_2, using a five reaction mechanism. Authors indicate that best fits were obtained using values of k close to those measured for the self reactions of CH_2ClO_2 and CCl_3O_2 (which are almost identical) in the same laboratory (Catoire et al., 1994; 1996), and recommend that k is the average these determinations: $2.6 \times 10^{-13} \exp[(800 \pm 60)/T]$ cm^3 molecule^{-1} s^{-1} over the temperature range 273 K to 460 K, with k= $(3.8 \pm 1.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

(b) Experiments performed at pressures in the range 1.3 to 4 mbar. $CHCl_2O_2$ radicals were produced by the F + CH_2Cl_2 reaction, with subsequent addition of O_2. $CHCl_2O_2$ radicals were monitored indirectly by titration to NO_2 following reaction with excess NO, with LIF detection of NO_2. ClO radicals generated by the secondary chemistry were also titrated to NO_2 under the experimental conditions. k values were extracted by numerical simulation of the results, using an 11 reaction scheme to take account possible of secondary reactions.

(c) Photolysis of Cl_2 in the presence of CH_2Cl_2-O_2-N_2 mixtures. In situ monitoring of products by IR showed formation of HC(O)Cl as the dominant product as part of an efficient chain mechanism. $C(O)Cl_2$ was observed as a minor product. Listed quantum yield based on the reported quantum yield of 5.9 for HC(O)Cl formation.

(d) Photolysis of Cl_2 in the presence of CH_2Cl_2-O_2-N_2 mixtures. In situ monitoring of products by FTIR spectroscopy showed formation of HC(O)Cl as the dominant product as part of an efficient chain mechanism. $C(O)Cl_2$ was observed as a minor product. Listed quantum yield based on the reported quantum yield of 7.5 for HC(O)Cl formation.

(e) Photolysis of Cl_2 or F_2 in the presence of CH_2Cl_2-O_2-N_2 mixtures. In situ monitoring of products by FTIR spectroscopy showed formation of HC(O)Cl and $C(O)Cl_2$ with yields of ca. 85% and 5% respectively. No other primary products were detected.

(f) Flash photolysis of Cl_2 in the presence of CH_2Cl_2-O_2-N_2 mixtures over the temperature range 250 K to 325 K demonstrated efficient chain regeneration of $CHCl_2O_2$ in the system.

Preferred Values

k_2/k = 1.0 at 298 K.

Reliability

$\Delta (k_2/k) = ^{+0.0}_{-0.15}$ at 298 K.

Comments on Preferred Values

The reported dominant chain formation of HC(O)Cl from CH_2Cl_2 oxidation in a number of product studies (Sanhueza and Heicklen, 1975; Niki et al., 1980; Catoire et al., 1996) has established that the self-reaction of $CHCl_2O_2$ proceeds almost exclusively via formation of $CHCl_2O$ radicals (channel (2)), which decompose by elimination of Cl. This is also supported by the failure to detect $CHCl_2OH$ in all the product studies, which would otherwise provide evidence for channel (1). The efficient chain regeneration of $CHCl_2O_2$ radicals observed in the Cl_2-CH_2Cl_2-O_2-N_2 flash photolysis experiments of Catoire et al. (1996) is also consistent with the dominance of channel (2) over a wide temperature range.

The reported determinations of k (Catoire et al., 1996; Biggs et al., 1999) are subject to substantial uncertainties, owing to the complexity of the secondary chemistry. Catoire et al. (1996) report only a broad range for k at 300K, based on simulations of a complex system in which competitive removal of $CHCl_2O_2$ by reaction with HO_2 was occurring (see note (a) above). The discharge flow determination of Biggs et al. (1999) was complicated by indirect detection of $CHCl_2O_2$ (which also had contributions from ClO), and possible secondary chain removal of $CHCl_2O_2$ via reactions with Cl and ClO. Consequently, no firm recommendation for k is currently possible, and further kinetics studies are required.

References

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Sanhueza, E. and Heicklen, J.: J. Phys. Chem. 79, 7, 1975.

IV.A2.215

$$\mathbf{CCl_3O_2 + CCl_3O_2 \rightarrow CCl_3O + CCl_3O + O_2}$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.6×10^{-12} $(T/298)^{-(3.0\pm1.0)}$	253-333	Danis et al., 1991	FP-UVA (a,b)
3.3×10^{-13} exp[$(745 \pm 58)/T$]	273-460	Catoire et al., 1996	FP-UVA (a,c)
$(4.07 \pm 0.54) \times 10^{-12}$	298		

Comments

(a) k is defined by -d[CCl_3O_2]/dt = 2k[CCl_3O_2]^2.

(b) Flash photolysis of Cl_2 in the presence of $CHCl_3$-O_2-N_2 mixtures at 1013 mbar total pressure. k was determined from the formation of C(O)Cl_2, using UV absorption spectroscopy at 240 nm. Results were consistent with chain formation of C(O)Cl_2, resulting from thermal decomposition of CCl_3O to generate C(O)Cl_2 and regenerate Cl.

(c) Flash photolysis of Cl_2 in the presence of $CHCl_3$-O_2-N_2 mixtures at 1013 mbar total pressure. k was determined from time-resolved UV absorption at 230 nm, 240 nm and 250 nm, which was dominated by formation of C(O)Cl_2 as part of an efficient chain mechanism. Results were consistent with a chain length of ca. 100. FTIR product studies of the photolysis of Cl_2-$CHCl_3$-O_2-N_2 mixtures and F_2-$CHCl_3$-O_2-N_2 mixtures also demonstrated 100% formation of C(O)Cl_2.

Preferred Values

$k = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.3 \times 10^{-13}$ exp$(740/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270-460 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The reported formation of C(O)Cl_2 with 100% yield from $CHCl_3$ oxidation in a number of product studies (Jayanty et al., 1975; Ohta and Mizoguchi, 1980; Catoire et al., 1996) has established that the self-reaction of CCl_3O_2 proceeds exclusively via formation of CCl_3O radicals, which decompose by elimination of Cl. This is also supported by the kinetics study of Catoire et al. (1996), involving flash photolysis-UV absorption of Cl_2 in the presence of $CHCl_3$ and O_2. The results demonstrate essentially quantitative regeneration of Cl atoms in the system, the chain length for conversion of $CHCl_3$ into C(O)Cl_2 being ca. 100.

The preferred values are based on the results of Catoire et al. (1996), which supersede those of Danis et al. (1991) (also cited in Russell et al., 1990) performed in the same laboratory. Catoire et al. (1996) demonstrated that the smaller formation rate of C(O)Cl_2 and shorter chain lengths observed in the earlier study (Danis et al., 1991) resulted from traces of ethanol which are invariably present in commercial samples of the reagent $CHCl_3$. Ethanol is three orders of magnitude more reactive than $CHCl_3$ towards Cl, and can therefore scavenge a proportion of Cl atoms when present in trace amounts.

References

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IV.A2.216

$$\begin{aligned} \mathbf{CH_3CHClO_2 + CH_3CHClO_2} &\rightarrow \mathbf{CH_3CHClOH + CH_3COCl + O_2} \quad &\mathbf{(1)} \\ &\rightarrow \mathbf{2CH_3CHClO + O_2} \quad &\mathbf{(2)} \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.2 \pm 1.3) \times 10^{-12}$	295	Maricq et al., 1993	(a,b)
Branching Ratios			
$k_2/k = 0.95 \pm 0.05$	295	Maricq et al., 1993	(b)

Comments

(a) k is defined by $-d[CH_3CHClO_2]/dt = 2k[CH_3CHClO_2]^2$.

(b) Pulsed photolysis of Cl_2 in the presence of C_2H_5Cl-O_2-N_2 mixtures with time-resolved IR spectral photography and transient diode laser absorption measurements. The above rate coefficient and branching ratio were obtained from the time-dependence and magnitude of the secondary HCl rise, by computer simulations involving a mechanism of 24 reactions.

Preferred Values

$k_2 = 5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.95$ at 298 K.

Reliability

$\Delta \log k_2 = \pm 0.3$ at 298 K.
$\Delta (k_2/k) = \pm 0.05$ at 298 K.

Comments on Preferred Values

While the data of Maricq et al. (1993) for the room temperature rate coefficient seem reasonable in relation to the values of other related halogen-containing peroxy radicals, they have been obtained from very indirect measurements. Confirmation by independent measurements is required to lower the recommended error limits.

References

Maricq, M. M., Shi, J., Szente, J. J., Rimai, L. and Kaiser, E. W.: J. Phys. Chem. 97, 9686, 1993.

IV.A2.217

$$\begin{aligned} \mathbf{CH_2ClCH_2O_2 + CH_2ClCH_2O_2} &\rightarrow \mathbf{CH_2ClCH_2OH + CH_2ClCHO + O_2} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{CH_2ClCH_2O + CH_2ClCH_2O + O_2} \quad \mathbf{(2)} \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_{obs} = 1.1 \times 10^{-13} \exp[(1020 \pm 170)/T]$	228-380	Dagaut et al., 1988	FP-UVA (a,b)
$k_{obs} = (3.57 \pm 0.57) \times 10^{-12}$	298		
$k_{obs} = (6.0 \pm 0.8) \times 10^{-12}$	295	Maricq et al., 1993	FP-UVA (a,c)
$k_{obs} = 4.0 \times 10^{-14} \exp[(1376 \pm 60)/T]$	253-345	Chakir et al., 2003	MM-UVA (a,d)
$k_{obs} = (4.5 \pm 0.4) \times 10^{-14}$			
Branching Ratios			
$k_1/k = 0.31$	295	Wallington et al., 1990	UV-P-FTIR (e)
$k_2/k = 0.69$			
$k_1/k = 0.43$	296	Yarwood et al., 1992	UV-P-FTIR (e)
$k_2/k = 0.57$			

Comments

(a) k_{obs} is based on the measured overall second-order decay of $CH_2ClCH_2O_2$, defined by $-d[CH_2ClCH_2O_2]/dt = 2k_{obs}[CH_2ClCH_2O_2]^2$. As described in detail by Lesclaux (1997), HO_2 radicals formed from the subsequent chemistry of CH_2ClCH_2O (formed from channel (2)) are expected to lead to secondary removal of $CH_2ClCH_2O_2$. The true value of k is expected to fall in the range $k_{obs}/(1 + \alpha) < k < k_{obs}$, where $\alpha = k_2/k$.

(b) Flash photolysis of Cl_2 in the presence of C_2H_4-O_2-N_2 mixtures over the pressure range 33–533 mbar. $CH_2ClCH_2O_2$ concentrations measured by UV absorption spectroscopy using $\sigma_{250\ nm} = (3.64 \pm 0.39) \times 10^{-18}$ cm^2 molecule^{-1}.

(c) Pulsed photolysis of Cl_2 in the presence of C_2H_4-O_2-N_2 mixtures at 1013 mbar pressure. Kinetics determined from time-resolved UV absorption spectra of $CH_2ClCH_2O_2$ and HO_2. The values of $\sigma(CH_2ClCH_2O_2)$ obtained are ca. 13% greater than those reported by Dagaut et al. (1988).

(d) Modulated photolysis of Cl_2 in the presence of C_2H_4-O_2-N_2 mixtures over the pressure range 67–267 mbar. k_{obs} determined from analysis of modulated absorption waveforms in the wavelength range 215–270nm. The UV absorption spectrum of $CH_2ClCH_2O_2$ characterized simultaneously, agrees well with that of Dagaut et al. (1988) at $\lambda \geq 240$ nm, with $\sigma_{250\ nm} = (3.56 \pm 0.20) \times 10^{-18}$ cm^2 molecule^{-1}. At shorter wavelengths, cross sections are up to 20% greater.

(e) Steady-state photolysis of Cl_2-C_2H_4-O_2-N_2 mixtures at total pressures of 933 mbar with FTIR spectroscopic monitoring of the removal of C_2H_4 and the formation of CH_2ClCHO, CH_2ClCH_2OOH, and CH_2ClCH_2OH. The listed branching ratios were derived from the yields of CH_2ClCH_2OH and CH_2ClCHO relative to the decay of C_2H_4.

Preferred Values

$k = 3.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.2 \times 10^{-14} \exp(1300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-380 K.
$k_1/k = 0.37$ at 298 K.
$k_2/k = 0.63$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 500$ K.
$\Delta (k_1/k) = \Delta (k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The studies of Wallington et al. (1990) and Yarwood et al. (1992) provide reasonably consistent determinations of k_2/k and the preferred value at 298 K is the average of these determinations. Chakir et al. (2003) also used steady state concentrations of HO_2 and $CH_2ClCH_2O_2$, inferred from their modulated photolysis study, to draw conclusions about the temperature dependence of the branching ratio for HO_2 formation, k_2/k. Using the 298 K values of Wallington et al. (1990) and Yarwood et al. (1992) as a reference, they estimated that k_2/k varies from ca. 0.3 at 253 K to ca. 0.7–0.9 at 345 K. k_2/k is expected to tend to unity as T increases.

The preferred values of k were calculated from the reported values of $k_{\rm obs}$ and k_2/k using a methodology similar to that employed by Lesclaux (1997) for peroxy radicals with self reaction rate coefficients $\geq$ ca. 2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at room temperature. k is estimated to be $k_{\rm obs}/(1 + 0.5(k_2/k))$, with this approximation assuming that the secondary reaction of HO_2 with $CH_2ClCH_2O_2$ competes equally with its removal via $HO_2 + HO_2$. The preferred values are based on the temperature dependence kinetics results of Dagaut et al. (1988) and Chakir et al. (2003), and the preferred value of k_2/k at 298 K, with the assumption that k_2/k increases to ≈ 1 at the high end of the studied temperature range, 380 K. The 298 K value of $k_{\rm obs}$ reported by Maricq et al. (1993) is ca. 50% greater than the average of the values of Dagaut et al. (1988) and Chakir et al. (2003), but is encompassed by the uncertainty range in the preferred value. The discrepancy is not fully resolved, but is partially explained by the greater absorption cross-sections for $CH_2ClCH_2O_2$ reported by Maricq et al. (1993).

References

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IV.A2.218

$O_3 + C_2HCl_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$< 3 \times 10^{-20}$	296	Atkinson et al., 1982	S-CL

Preferred Values

$k < 5 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The upper limit to the preferred value is taken from the data of Atkinson et al. (1982), with the upper limit being increased by a factor of ∼2 to take into account additional uncertainties in the study of Atkinson et al. (1982). This upper limit is consistent with the reported data for the reactions of O_3 with the chloroethenes (Atkinson and Carter, 1984), which show that Cl atom substitution markedly decreases the rate coefficients at room temperature, relative to that for ethene.

References

Atkinson, R. and Carter, W. P. L.: Chem. Rev., 84, 437, 1984.
Atkinson, R., Aschmann, S. M., Fitz, D. R., Winer, A. M. and Pitts, J. N. Jr.: Int. J. Chem. Kinet., 14, 13, 1982.

IV.A2.219

$O_3 + C_2Cl_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$< 2 \times 10^{-23}$	297	Mathias et al., 1974	(a)

(a) From experiments carried out at initial O_3 and tetrachloroethene concentrations of $\geq 10^{17}$ molecule cm^{-3} in the presence of excess O_2, using an assumed mechanism and monitoring the formation rate of $C(O)Cl_2$. From the data given in Mathias et al. (1974), a more conservative upper limit of $k < 8 \times 10^{-23}$ cm^3 molecule^{-1} s^{-1} can be derived by assuming that only one $C(O)Cl_2$ molecule is formed per tetrachloroethene reacted.

Preferred Values

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

Comments on Preferred Values

The upper limit to the preferred value is derived from the very limited amount of data reported by Mathias et al. (1974), with the upper limit to the rate coefficient being increased by a factor of 50 over that reported. This upper limit to the rate coefficient for tetrachloroethene is consistent with the kinetic data for the other chloroethenes (Atkinson and Carter, 1984), which show that Cl atom substitution markedly decreases the reactivity of the chloroethenes towards O_3, compared to that for ethene.

References

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IV.A2.220

$CH_3Cl + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$CH_3Cl + h\nu \rightarrow CH_3 + Cl$	349	343

Preferred Values

Absorption cross-sections for CH_3Cl at 295 K and 210 K

λ/nm	$10^{20}\ \sigma/cm^2$ 295 K[a]	λ/nm	$10^{20}\sigma/cm^2$ 295 K	$10^{20}\sigma/cm^2$ 210 K
174	111	198	2.66	2.43
176	93.8	200	1.76	1.51
178	76.6	202	1.13	0.93
180	60.7	204	0.750	0.573
182	46.7	206	0.483	0.345
184	35.0	208	0.318	0.212
186	25.5	210	0.206	0.130
188	18.2	212	0.132	0.080
190	12.7	214	0.086	0.047
192	8.72	216	0.055	0.027
194	5.88			
196	4.01			

[a] No temperature dependence at $\lambda < 198$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K and at 210 K are those reported by Simon et al. (1988). This latter publication reports the results of the most comprehensive study of the temperature dependence. These values are in very good agreement with the room temperature values reported by Robbins (1976) and are in reasonable agreement with the results of Hubrich et al. (1977) who also made low temperature measurements. In the wavelength region 180–216 nm, photolysis occurs with unit quantum efficiency by breaking of the C-Cl bond to yield CH_3 + Cl. Photochemistry at shorter wavelengths is discussed by Shold and Rebbert (1978). A H-atom product channel has now been observed using product translational energy studies (Amaral et al., 2001).

References

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IV.A2.221

$CH_3OCl + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$CH_3OCl + h\nu$	$\rightarrow CH_3O + Cl$	(1)	202.9	589
	$\rightarrow CH_3 + ClO$	(2)	312.4	383
	$\rightarrow CH_2OCl + H$	(3)	417.4	287

Absorption cross-sections for CH_3Cl at 295 K and 210 K

Wavelength/nm	Reference	Comments
200-460	Crowley et al., 1994	(a)
230-394	Jungkamp et al., 1995	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength region/nm	Reference	Comments
$\phi_1 = 0.95 \pm 0.05$	308	Schindler et al., 1997	(c)
$\phi_1 = 1$	248	Krisch et al., 2004	(d)

Comments

(a) Monochromator/diode array set up with spectral resolution of 0.4 nm. The spectrum measured at 295 K showed no dependence on resolution between 0.3 and 1.2 nm. Correction applied for small Cl_2 impurities which were quantified by MS.

(b) Monochromator/double diode array set up (temperature and resolution not quoted). Impurities (CH_3OH and Cl_2) quantified by MS.

(c) Pulsed laser photolysis (excimer at 308 nm, dye laser at 235 nm) with REMPI-TOF mass spectrometric detection of Cl photofragments in both $^2P_{1/2}$ and $^2P_{3/2}$ states. The overall quantum yield of Cl atom generation at 308 nm was measured relative to Cl_2. The ratio of Cl ($^2P_{1/2}$) / Cl ($^2P_{3/2}$) was found to be 0.31 ± 0.02 at 308 nm and 1.45 ± 0.05 at 235 nm.

(d) Crossed laser-molecular beam scattering experiment with detection of photofragments by VUV photoionisation-TOFMS (Cl detected as Cl^+ and CH_3O as CHO^+). No other photofragments were observed.

Preferred Values

Absorption cross-sections for CH_3OCl at 295 K

λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\sigma/\mathrm{cm}^2$
200	6.61	340	0.908
210	5.41	350	0.649
220	10.0	360	0.441
230	16.1	370	0.296
240	16.6	380	0.203
250	11.5	390	0.144
260	6.00	400	0.108
270	2.75	410	0.082
280	1.56	420	0.064
290	1.35	430	0.048
300	1.44	440	0.037
310	1.49	450	0.027
320	1.39	460	0.020
330	1.18		

Quantum yields

ϕ_1 = 1.0 throughout the absorption spectrum

Comments on Preferred Values

There is very good agreement between the cross sections presented in both studies for $\lambda > 260$ nm, (Crowley et al., 1994; Jungkamp et al., 1995) though some differences are observed at the short wavelength end of the spectra. The data of Crowley et al. (1994), which cover a larger wavelength range and extend further into the actinic region are preferred. The preferred overall quantum yield of 1.0 is based on the work of Schindler et al. (1997), which is consistent with the observations of Krisch et al. (2004) and with quantum yields measured for other hypohalites such as HOCl.

References

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IV.A2.222

$CHF_2Cl + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$CHF_2Cl + h\nu$	$\rightarrow CHF_2 + Cl$	(1)	327	327
	$\rightarrow CClF_2 + H$	(2)	423	283
	$\rightarrow CF_2 + HCl$	(3)	207	287

Absorption cross-sections for CHF_2Cl at 298 K and 210 K

λ/nm	$10^{20}\ \sigma$/cm^2 298 K[a]	λ/nm	$10^{20}\sigma$/cm^2 298 K	$10^{20}\ \sigma$/cm^2 210 K
174	5.72	188	0.372	0.372
176	4.04	190	0.245	0.242
178	2.76	192	0.156	0.148
180	1.91	194	0.103	0.093
182	1.28	196	0.072	0.062
184	0.842	198	0.048	0.039
186	0.576	200	0.032	0.0159
		202	0.022	0.0159
		204	0.014	0.0096

[a] No temperature dependence at $\lambda < 188$ nm.

Quantum yields for CHF_2Cl photolysis

$\phi(1) = 0.84$; $\phi(2) = 0.16$ at 193 nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are those reported by Simon et al. (1988). In the same study (Simon et al., 1988) the temperature dependence down to 210 K has been reported, with the values at the shorter wavelengths being temperature-independent within the precision of the measurements. The values at longer wavelengths show a decrease as the temperature is lowered (Simon et al., 1988). These results are in reasonable agreement with those of earlier studies cited in NASA, 1997. Melchior et al. (1996) studied the photodissociation of CHF_2Cl at 193 nm using TOF-MS combined with 2+1 REMPI to detect products. Photolysis by 2 channels, C-Cl and C-H bond rupture, was observed; HCl elimination was not found. C-Cl rupture is the main channel. The minor channel yield was $\phi_H/\phi_{total} = 0.16 \pm 0.05$. This work forms the basis of the recommended values at 193 nm. The quantum yields are likely to be wavelength dependent with $\phi(1)$ increasing towards 1.0 at the absorption threshold near 205 nm.

References

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IV.A2.223

$CF_2Cl_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$CF_2Cl_2 + h\nu$	$\rightarrow CF_2Cl + Cl$	(1)	346	346
	$\rightarrow CF_2 + 2Cl$	(2)	542	221

Absorption cross-sections for CF_2Cl_2 at 295 K and 210 K

λ/nm	10^{20} σ/cm^2 295 K	10^{20} σ/cm^2 210 K^a	λ/nm	10^{20}σ/cm^2 295 K	10^{20} σ/cm^2 210 K
174	162		200	8.89	5.11
176	181		202	5.51	2.97
178	187		204	3.44	1.69
180	179		206	2.09	0.99
182	160		208	1.27	0.56
184	134		210	0.76	0.32
186	107		212	0.45	0.18
188	82.8	79.3	214	0.27	0.10
190	63.2	52.9	216	0.16	0.058
192	45.5	35.8	218	0.10	0.033
194	31.5	22.8	220	0.060	0.018
196	21.1	14.4	222	0.036	0.010
198	13.9	8.8	224	0.022	0.006
			226	0.013	0.003

[a] No temperature dependence at $\lambda \leq 186$ nm.

Quantum yields for CF_2Cl_2 photolysis at 298K

$\phi(1) = 1$ over the range 190–225 nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K and at 210 K are those reported by Simon et al. (1988). This publication reports the results of the most comprehensive study of the temperature dependence (Simon et al., 1988). The values at room temperature are in good agreement with those recommended in our previous evaluation, CODATA, 1980, where a detailed discussion of earlier work can be found. They also agree with the recommendations of NASA (1997) which include an expression for the temperature dependent cross-sections applicable over the range 190–210 nm:

$$\sigma_T = \sigma(218)\exp\{4.1\times10^{-4}\ (\lambda - 184.9)(T\text{-}298)\}\ [\lambda \text{ in nm; } T \text{ in K}].$$

More recently the absorption cross-sections of CF_2Cl_2 at 298 K have been measured over the range $225< \lambda <110$ nm using synchrotron radiation (Limao Vieira et al., 2002). The results agree well with those recommended by IUPAC in the overlapping wavelength range.

Baum and Huber (1993) studied laser photodissociation of CF_2Cl_2 at 193 nm, with photoproducts investigated by TOF-MS. Results show exclusive dissociation to CF_2Cl + Cl, with the CF_2Cl fragment containing insufficient energy for prompt dissociation to produce a second Cl atom. This is contrary to the earlier suggestion by Rebbert and Ausloos (1975) that formation of 2 Cl atoms occurred with increasing tendency at wavelengths $<$ 230 nm. For the purposes of atmospheric photolysis a value of $\phi(1) = 1$ is recommended.

References

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IV.A2.224

$CFCl_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ.mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CFCl_3 + h\nu$	$\rightarrow CFCl_2 + Cl$	(1)	317	377
	$\rightarrow CFCl + 2Cl$	(2)	558	214

Absorption cross-sections for $CFCl_3$ at 295 K and 210 K

λ/nm	$10^{20}\ \sigma$/cm^2 295 K	$10^{20}\ \sigma$/cm^2 210 K[a]	λ/nm	$10^{20}\sigma$/cm^2 295 K	$10^{20}\ \sigma$/cm^2 210 K
174	313		210	14.8	9.9
176	324		212	10.5	6.63
178	323		214	7.56	4.31
180	314		216	5.38	2.78
182	296		218	3.79	1.77
184	272		220	2.64	1.13
186	243	230	222	1.82	0.71
188	213	202	224	1.24	0.45
190	179	170	226	0.84	0.29
192	154	141	228	0.56	0.19
194	124	115	230	0.37	0.12
196	99.1	90.5	235	0.126	
198	78.0	71.8	240	0.046	
200	64.5	55.8	245	0.017	
202	50.0	42.0	250	0.0066	
204	37.4	30.0	255	0.0034	
206	28.0	21.6	260	0.0015	
208	19.7	14.9			

[a] No temperature dependence at $\lambda \leq 184$ nm.

Quantum yields for $CFCl_3$ photolysis at 298K

$\phi(1) = 1$ at $\lambda > 180$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections for 174–250 nm at 295 K and 210 K are the values reported by Simon et al. (1988). This publication reports the results of the most comprehensive study of the temperature dependence (Simon et al., 1988). For $\lambda > 230$ nm, the absorption cross-section values are those reported by Hubrich and Stuhl (1980). The values are in good agreement with those recommended in our previous evaluation, CODATA, 1982, where a detailed discussion of earlier work can be found. They also agree with the recommendations of NASA (1997) which include an expression for the temperature dependent cross-sections applicable over the range 190–210 nm:

$$\sigma_T = \sigma(218)\exp\{4.1\times 10^{-4}\ (\lambda\text{-}184.9)(T\text{-}298)\}\ [\lambda \text{ in nm; } T \text{ in K}].$$

Felder and Demuth (1993) studied laser photodissociation of $CFCl_3$ at 193 nm using TOF-MS to investigate the nature and energetics of the photofragments. At this wavelength dissociation occurs exclusively to yield $CFCl_2 + Cl$ products. This result is in conflict with the earlier conclusions of Rebbert and Ausloos (1975) that $\phi(2)$ increases from 0.06 at 220 nm to 0.43 at 170 nm. This result from indirect experiments must now be considered dubious.

References

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IV.A2.225

$CCl_4 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$CCl_4 + h\nu$	$\rightarrow CCl_3 + Cl$	(1)	288	415
	$\rightarrow CCl_2 + 2Cl$	(2)	577	207

Preferred Values

Absorption cross-sections for CCl_4 at 295 K and 210 K

λ/nm	$10^{20}\ \sigma/cm^2$ 295 K	$10^{20}\ \sigma/cm^2$ 210 K[a]	λ/nm	$10^{20}\sigma/cm^2$ 295 K	$10^{20}\ \sigma/cm^2$ 210 K
174	990		220	17.5	12.5
176	1010		222	13.6	9.0
178	975		224	10.2	6.4
180	720		226	7.6	4.4
182	590		228	5.6	3.16
184	440		230	4.28	2.27
186	310		232	3.04	1.52
188	198		234	2.20	1.05
190	147		236	1.60	0.72
192	99.2		238	1.16	0.50
194	76.7		240	0.830	0.234
196	69.5		242	0.590	0.234
198	68.0		244	0.413	0.158
200	66.0		246	0.290	0.108
202	63.8		248	0.210	0.076
204	61.0	60.1	250	0.148	0.053
206	57.0	54.4	255	0.066	
208	52.5	48.3	260	0.025	
210	46.9	41.5	265	0.013	
212	41.0	34.8	270	0.006	
214	34.5	27.9	275	0.002	
216	27.8	21.7			
218	22.1	16.3			

[a] No temperature dependence at $\lambda < 204$ nm.

Quantum yields for CCl_4 photolysis at 298K

$\phi(1) = 1$ over wavelength range 174–275 nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections for 174–230 nm at 295 K and 210 K are the values reported by Simon et al. (1988). This recent publication reports the results of the most comprehensive study of the temperature dependence Simon et al. (1988). For $\lambda > 230$ nm, the absorption cross-section values are those reported by Hubrich and Stuhl (1980). The values at room temperature are in good agreement with those recommended in our previous evaluation, CODATA, 1982, where a detailed discussion of earlier work can be found. Photodissociation via C-Cl bond fission expected to occur with unit quantum yield. There is also evidence for direct release of a second Cl atom (channel 2) at $\lambda < 220$ nm. The earlier results of Rebbert and Ausloos (1976/77) are now supported by pulsed laser photolysis experiments at 193 nm and 135 nm which give ϕ(Cl) = 1.5 ± 0.1 and 1.9 ± 0.1 respectively at these wavelengths (Hanf et al., 2003).

References

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IV.A2.226

$CH_3CF_2Cl + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CF_2Cl + h\nu$	$\rightarrow CH_3CF_2 + Cl$	335 (est)	360
	$\rightarrow CH_2CF_2Cl + H$	400 (est)	300

Preferred Values

Absorption cross-sections for CH_3CF_2Cl at 298 K and 220 K

λ/nm	$10^{20}\ \sigma$/cm^2 298 K	$10^{20}\ \sigma$/cm^2 220 K	λ/nm	$10^{20}\sigma$/cm^2 298 K	$10^{20}\ \sigma$/cm^2 220 K
190	1.01	0.75	210	0.017	0.010
192	0.69	0.51	212	0.010	0.006
194	0.49	0.34	214	0.007	0.003
196	0.33	0.22	216	0.004	0.002
198	0.22	0.15	218	0.003	0.001
200	0.14	0.091	220	0.002	0.0007
202	0.09	0.057	222	0.0009	0.0004
204	0.061	0.037	224	0.0005	0.0002
206	0.039	0.024	226	0.0003	0.0001
208	0.026	0.015	228	0.0002	0.0001

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon (1991), Orlando et al. (1991) and (for 190–210 nm) Nayak et al. (1996). The agreement between these studies over the wavelength range of preferred values is good. The results of Hubrich and Stuhl (1980) are in reasonable agreement. The temperature dependence down to about 220 K has been reported by Gillotay and Simon (1991), Orlando et al. (1991) and Nayak et al. (1996). The preferred values at 220 K for the wavelength range 190 nm to 210 nm are the mean of the values reported by Gillotay and Simon (1991), Orlando et al. (1991) and Nayak et al. (1996). Because Nayak et al. (1996) did not report values for $\lambda > 210$ nm at their lowest temperature of 223 K, and the values of Orlando et al. (1991) at wavelengths greater than approximately 210 nm have been questioned (Gillotay and Simon, 1991; Nayak et al., 1996), the preferred values at 220 K and $\lambda > 210$ nm are the values reported by Gillotay and Simon (1991). Photolysis is expected to occur with unit quantum efficiency. At 193 nm Melchior et al. (1997) have shown that C-Cl bond fission to give CH_3CF_2 + Cl is the main channel, but that C-H bond cleavage also occurs with a branching ratio of about 40%.

References

Gillotay, D. and Simon, P. C.: J. Atmos. Chem. 12, 269, 1991.
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Melchior, A., Bar, I. and Rosenwaks, S.: J. Chem. Phys. 107, 8476, 1997.
Nayak, A.K., Buckley, T. J., Kurylo, M. J. and Fahr, A.: J. Geophys. Res. 101, 9055, 1996.
Orlando, J. J., Burkholder, J. B., McKeen, S. A. and Ravishankara, A. R.: J. Geophys. Res. 96, 5013, 1991.

IV.A2.227

CH_3CFCl_2 + hν → products

Primary photochemical processes

Reaction		$\Delta H°$/kJ.mol^{-1}	$\lambda_{\text{threshold}}$/nm
CH_3CFCl_2 + hν	→ CH_3CFCl + Cl	335 (est)	360
	→ CH_2CFCl_2 + H	400 (est)	300

Preferred Values

Absorption cross-sections for CH_3CFCl_2 at 298 K and 210 K

λ/nm	$10^{20}\ \sigma$/cm^2 298 K	$10^{20}\ \sigma$/cm^2 210 K	λ/nm	$10^{20}\sigma$/cm^2 298 K	$10^{20}\ \sigma$/cm^2 210 K
190	83.8	80.1	210	2.1	1.6
192	64.1	59.5	212	1.4	1.0
194	47.4	42.8	214	0.88	0.65
196	34.0	30.0	216	0.57	0.41
198	23.8	20.6	218	0.37	0.26
200	16.4	13.8	220	0.24	0.16
202	11.1	9.2	222	0.16	0.10
204	7.4	6.0	224	0.10	0.06
206	4.9	3.9	226	0.07	0.04
208	3.2	2.5	228	0.04	0.03

Comments on Preferred Values

The preferred values of the absorption cross sections at 298 K are the values reported by Fahr et al. (1993). In this study (Fahr et al., 1993), measurements were made in the gas phase (190–260 nm) and the liquid phase (230–260 nm) at 298 K. Correction factors were used to convert these liquid-phase values into accurate gas-phase values at the long wavelengths. Results reported in this study (Fahr et al., 1993) are in very good agreement with those reported by Gillotay and Simon (1991). The results of Talukdar et al. (1991) are lower at shorter wavelengths and higher at longer wavelengths. Gillotay and Simon (1991) and Talukdar et al. (1991) report the temperature dependence down to 210 K. The low temperature values of Gillotay and Simon (1991) are preferred, and their 210 K values are given in the table. Photolysis is expected to occurwith unit quantum efficiency. At 193 nm Melchior et al. (1997) have shown that C-Cl bond fission to give CH_3CFCl + Cl is the main channel, but that C-H bond cleavage also occurs with a branching ratio of about 15%. H atom formation is also observed at 205-209 nm using the photofragment velocity map imaging technique (Mashino et al., 2005).

References

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Gillotay, D. and Simon, P. C.: J. Atmos. Chem. 12, 269, 1991.
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IV.A2.228

$CH_3CCl_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CCl_3 + h\nu$	$\rightarrow CH_3CCl_2 + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for CH_3CCl_3 at 295 K and 210 K

λ/nm	$10^{20}\ \sigma$/cm^2 295 K	$10^{20}\ \sigma$/cm^2 210 K	λ/nm	$10^{20}\sigma$/cm^2 295 K	$10^{20}\ \sigma$/cm^2 210 K
182	315	a	210	24.0	19.8
184	280	a	212	16.8	13.2
186	250	a	214	12.0	8.8
188	220	a	216	8.6	6.1
190	192	a	218	6.0	4.2
192	163	a	220	4.1	2.9
194	140	a	222	2.9	1.2
196	118	a	224	2.0	1.2
198	99	a	226	1.5	0.76
200	81	a	228	1.0	0.51
202	66	64	230	0.70	0.33
204	52	49	232	0.49	0.18
206	40	36	234	0.33	0.11
208	31	26	236	0.23	0.064
			238	0.15	0.036
			240	0.10	0.024

(a) No temperature dependence observed.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K and at 210 K are the values reported by Vanlaethem-Meuree et al. (1979), who determined absorption cross-section values at 295 K, 270 K, 250 K, 230 K and 210 K for the wavelength range 180–240 nm. These values (Vanlaethem-Meuree et al., 1979) are preferred over the substantially higher values reported by Hubrich and Stuhl (1980), in which study a correction was required for the presence of the UV-absorbing stabilizer 1,4-dioxane. In a recent study, Nayak et al. (1995) reported measurements in the gas phase (160–240 nm) and the liquid phase (235–260 nm) over the temperature range 220–330 K. A wavelength shift procedure was used to convert the liquid-phase values into effective gas-phase values at the long wavelengths. The reported room temperature values of Nayak et al. (1995) are in good agreement (within 15%) with those of Vanlaethem-Meuree et al. (1979) in the range 210–240 nm, whereas in the 180–210 nm range they are 15% to 30% higher. Low temperature results are in relatively good agreement up to 230 nm. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CH_3CCl_2 + Cl.

References

Hubrich, C. and Stuhl, F.: J. Photochem. 12, 93, 1980.
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IV.A2.229

$CF_3CHFCl + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$CF_3CHFCl + h\nu$	$\rightarrow CF_3CHF + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for CF_3CHFCl at 298 K and 210 K

λ/nm	$10^{20}\ \sigma$/cm^2 298 K	$10^{20}\ \sigma$/cm^2 210 K	λ/nm	$10^{20}\sigma$/cm^2 298 K	$10^{20}\ \sigma$/cm^2 210 K
190	0.77	0.62	210	0.018	0.010
192	0.55	0.42	212	0.012	0.006
194	0.39	0.29	214	0.008	0.004
196	0.27	0.19	216	0.006	0.003
198	0.18	0.13	218	0.004	0.002
200	0.13	0.084	220	0.003	0.0011
202	0.086	0.055	222	0.002	0.0007
204	0.060	0.036	224	0.002	0.0005
206	0.040	0.023	226	0.001	0.0003
208	0.027	0.015	228	0.001	0.0002

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the averages of the values reported by Orlando et al. (1991) and Gillotay and Simon (1991), which are in good agreement. Both studies investigated the temperature dependence down to about 210 K. The temperature dependences of Orlando et al. (1991) are greater for shorter wavelengths ($<$ 200 nm) and less for the longer wavelengths than those reported by Gillotay and Simon (1991). The low temperature values of Gillotay and Simon (1991) are preferred, and their 210 K values are given in the table. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF_3CHF + Cl.

References

Gillotay, D. and Simon, P. C.: J. Atmos. Chem. 13, 289, 1991.
Orlando, J. J., Burkholder, J. B., McKeen, S. A. and Ravishankara, A. R.: J. Geophys. Res. 96, 5013, 1991.

IV.A2.230

CF_3CHCl_2 + h$\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ.mol^{-1}	$\lambda_{\text{threshold}}$/nm
CF_3CHCl_2 + hν	$\rightarrow CF_3CHCl$ + Cl	335 (est)	360

Preferred Values

Absorption cross-sections for CF_3CHCl_2 at 298 K and 220 K

λ/nm	$10^{20}\ \sigma/\text{cm}^2$ 298 K	$10^{20}\ \sigma/\text{cm}^2$ 220 K	λ/nm	$10^{20}\sigma/\text{cm}^2$ 298 K	$10^{20}\ \sigma/\text{cm}^2$ 220 K
190	61.5	54.3	210	1.8	1.2
192	46.2	39.7	212	1.3	0.82
194	33.9	28.1	214	0.84	0.55
196	24.1	19.2	216	0.57	0.38
198	17.2	13.4	218	0.38	0.27
200	12.0	9.1	220	0.26	0.18
202	8.3	6.1	222	0.18	0.13
204	5.7	4.1	224	0.12	0.09
206	3.9	2.7	226	0.09	0.06
208	2.7	1.8	228	0.06	0.04

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon (1991), Orlando et al. (1991) and Nayak et al. (1996). The agreement between these studies over the wavelength range of preferred values is very good. The temperature dependence down to about 220 K has been reported by Gillotay and Simon (1991), Orlando et al. (1991) and Nayak et al. (1996). The preferred values at 220 K for the wavelength range 190 nm to 220 nm are the mean of the values reported by Gillotay and Simon (1991), Orlando et al. (1991) and Nayak et al. (1996). Because Nayak et al. (1996) did not report values for $\lambda > 220$ nm at their lowest temperature of 223 K, and the values of Orlando et al. (1991) at wavelengths greater than approximately 220 nm have been questioned (Gillotay and Simon, 1991; Nayak et al., 1996), the preferred values at 220 K and $\lambda > 220$ nm are the values reported by Gillotay and Simon (1991). Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF_3CHCl + Cl.

References

Gillotay, D. and Simon, P. C.: J. Atmos. Chem. 12, 269, 1991.
Nayak, A. K., Buckley, T. J., Kurylo, M. J. and Fahr, N.: J. Geophys. Res. 101, 9055, 1996.
Orlando, J. J., Burkholder, J. B., McKeen, S. A. and Ravishankara, A. R.: J. Geophys. Res. 96, 5013, 1991.

IV.A2.231

$CF_2ClCFCl_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$CF_2ClCFCl_2 + h\nu$	$\rightarrow CF_2ClCFCl + Cl$	(1)	346 (est)	346
	$\rightarrow CFCl_2CF_2 + Cl$	(2)	346 (est)	346

Preferred Values

Absorption cross-sections for $CF_2ClCFCl_2$ at 295 K and 210 K

λ/nm	$10^{20}\ \sigma/cm^2$ 295 K	$10^{20}\ \sigma/cm^2$ 210 K	λ/nm	$10^{20}\sigma/cm^2$ 295 K	$10^{20}\ \sigma/cm^2$ 210 K
184	118	a	210	1.80	1.12
186	104	a	212	1.15	0.696
188	83.5	a	214	0.760	0.452
190	64.5	a	216	0.505	0.298
192	48.8	a	218	0.318	0.184
194	36.0	a	220	0.220	0.125
196	26.0	24.3	222	0.145	0.081
198	18.3	15.9	224	0.095	0.053
200	12.5	10.1	226	0.063	0.034
202	8.60	6.54	228	0.041	0.022
204	5.80	4.09	230	0.027	0.014
206	4.00	2.66			
208	2.65	1.68			

(a) No temperature dependence observed.

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Simon et al. (1988). They are in good agreement with the room temperature results of Chou et al. (1978) and Hubrich and Stuhl (1980), who also made low temperature measurements. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield $CF_2ClCFCl + Cl$ or $CFCl_2CF_2 + Cl$.

References

Chou, C. C., Milstein, R. J., Smith, W. S., Vera Ruiz, H., Molina, M. J. and Rowland, F. S.: J. Phys. Chem. 82, 1, 1978.
Hubrich, C. and Stuhl, F.: J. Photochem. 12, 93, 1980.
Simon, P. C., Gillotay, D., Vanlaethem-Meuree, N. and Wisemberg, J.: Ann. Geophysicae 6, 239, 1988.

IV.A2.232

$CF_2ClCF_2Cl + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ.mol^{-1}	$\lambda_{threshold}$/nm
$CF_2ClCF_2Cl + h\nu$	$\rightarrow CF_2ClCF_2 + Cl$	346 (est)	346

Preferred Values

Absorption cross-sections for CF_2ClCF_2Cl at 295 K and 210 K

λ/nm	$10^{20}\ \sigma/cm^2$ 295 K	$10^{20}\ \sigma/cm^2$ 210 K	λ/nm	$10^{20}\sigma/cm^2$ 295 K	$10^{20}\ \sigma/cm^2$ 210 K
172	69	a	200	0.80	0.55
174	55	a	202	0.54	0.34
176	43	a	204	0.37	0.22
178	34	a	206	0.24	0.13
180	26	a	208	0.16	0.084
182	19.8	a	210	0.104	0.051
184	15.0	a	212	0.068	0.031
186	11.0	a	214	0.044	0.020
188	7.80	7.72	216	0.029	0.012
190	5.35	5.03	218	0.019	0.007
192	3.70	3.28	220	0.012	0.004
194	2.56	2.13			
196	1.75	1.39			
198	1.20	0.88			

(a) No temperature dependence observed.

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Simon et al. (1988). They are in good agreement with the room temperature results of Chou et al. (1978). Hubrich and Stuhl (1980) reported higher values and a smaller temperature dependence. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF_2ClCF_2+ Cl.

References

Chou, C. C., Milstein, R. J., Smith, W. S., Vera Ruiz, H., Molina, M. J. and Rowland, F. S.: J. Phys. Chem. 82, 1, 1978.
Hubrich, C. and Stuhl, F.: J. Photochem. 12, 93, 1980.
Simon, P. C., Gillotay, D., Vanlaethem-Meuree, N. and Wisemberg, J.: Ann. Geophysicae 6, 239, 1988.

IV.A2.233

$CF_3CF_2Cl + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ.mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CF_3CF_2Cl + h\nu$	$\rightarrow CF_3CF_2 + Cl$	346	346

Preferred Values

Absorption cross-sections for CF_3CF_2Cl at 295 K to 225 K

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
172	5.65	190	0.27
174	4.05	192	0.19
176	2.85	194	0.13
178	2.05	196	0.090
180	1.45	198	0.063
182	1.05	200	0.044
184	0.75	202	0.031
186	0.53	204	0.021
188	0.38		

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Simon et al. (1988). In this study measurements were made down to 225 K, and the absorption cross-section values were found to be independent of temperature. They are in good agreement with the results of Hubrich and Stuhl (1980), who also made low temperature measurements. Earlier measurements of Chou et al. (1978) are 50% higher. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF_3CF_2 + Cl.

References

Chou, C. C., Milstein, R. J., Smith, W. S., Vera Ruiz, H., Molina, M. J. and Rowland, F. S.: J. Phys. Chem. 82, 1, 1978.
Hubrich, C. and Stuhl, F.: J. Photochem. 12, 93, 1980.
Simon, P. C., Gillotay, D., Vanlaethem-Meuree, N. and Wisemberg, J.: Ann. Geophysicae 6, 239, 1988.

IV.A2.234

$CF_3CF_2CHCl_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ.mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CF_3CF_2CHCl_2 + h\nu$	$\rightarrow CF_3CF_2CHCl + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for $CF_3CF_2CHCl_2$ at 298 K

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
160	269	200	16
165	197	205	6.9
170	183	210	2.9
175	191	215	1.2
180	177	220	0.46
185	129	225	0.17
190	74	230	0.065
195	37	240	0.011

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Braun et al. (1991). In the same study, absorption cross-section measurements in the liquid phase were made over the wavelength range 205–270 nm (Braun et al., 1991). Correction factors were used to convert these liquid-phase values into gas-phase values. The combined set of gas-phase values for the wavelength range 170–270 nm were fitted (Braun et al., 1991) with the expression:

$$\log_{10}\sigma = -17.966 + 4.542 \times 10^{-2}\ X - 2.036 \times 10^{-3}\ X^2 + 1.042 \times 10^{-5}\ X^3$$

where $X = (\lambda - 160\ \text{nm})$

Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield $CF_3CF_2CHCl + Cl$.

References

Braun, W., Fahr, A., Klein, R., Kurylo, M. J. and Huie, R. E.: J. Geophys. Res. 96, 13009, 1991.

IV.A2.235

CF_2ClCF_2CHFCl + hν → products

Primary photochemical processes

Reaction		$\Delta H°$/kJ mol^{-1}	λ threshold/nm
CF_2ClCF_2CHFCl + hν	→ CF_2ClCF_2CHF + Cl	335 (est)	360
	→ $CHFClCF_2CF_2$ + Cl	335 (est)	360

Preferred Values

Absorption cross-sections for CF_2ClCF_2CHFCl at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	$10^{20}\sigma$/cm^2
160	188	185	9.1
165	145	190	3.5
170	91	195	1.5
175	47	200	0.63
180	21	205	0.33
		210	0.25

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Braun et al. (1991). In the same study, absorption cross-section measurements in the liquid phase were made over the wavelength range 205–270 nm (Braun et al., 1991). Correction factors were used to convert these liquid-phase values into gas-phase values. The combined set of gas-phase values for the wavelength range 170–270 nm were fitted with the expression:

$$\log_{10}\sigma = -17.714 - 2.175 \times 10^{-2}\ X - 1.484 \times 10^{-3}\ X^2 + 1.147 \times 10^{-5}\ X^3$$

where $X = (\lambda - 160\ \text{nm})$

Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF_2ClCF_2CHF + Cl or $CHFClCF_2CF_2$ + Cl.

References

Braun, W., Fahr, A., Klein, R., Kurylo, M. J. and Huie, R. E.: J. Geophys. Res. 96, 13009, 1991.

IV.A2.236

HC(O)Cl + hν → products

Primary photochemical processes

Reaction		$\Delta H°$/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
HC(O)Cl + hν	→ HCO + Cl	340 (est)	350

Preferred Values

Absorption cross-sections for HC(O)Cl at the band maxima (298 K, 1013 mbar of N_2, spectral resolution 0.7 nm)

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
236.1	3.8	280.2	2.4
241.5	4.9	282.7	2.3
247.3	5.6	285.3	1.64
251.4	5.4	286.8	1.04
253.7	6.0	288.0	0.86
256.1	5.6	289.4	0.97
258.2	5.8	292.2	0.81
260.2	6.0	294.9	0.46
263.5	5.1	296.7	0.32
265.7	5.3	298.1	0.22
267.9	5.2	299.5	0.25
269.1	3.9	302.3	0.172
270.2	3.5	305.2	0.080
271.4	4.0	308.1	0.027
273.8	4.1	309.3	0.021
276.3	3.4	311.1	0.020
277.7	2.4	314.1	0.013
278.9	2.1	316.7	0.008
		318.7	0.007

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are those reported by Libuda et al. (1990). These are the values of the absorption cross-sections at the absorption maxima and were measured at a spectral resolution of 0.7 nm. The absorption bands for $\lambda > 265$ nm became distinctly sharper when the spectral resolution was improved to 0.4 nm. The spectrum of HC(O)Cl is similar to that of HCHO but is shifted to shorter wavelengths by 45 nm. Although there have been no quantum yield studies of HC(O)Cl photolysis, it is reasonable to assume by analogy with the photolysis of C(O)Cl_2 that the primary photolysis pathway proceeds by breaking of the C-Cl bond to yield HCO + Cl.

References

Libuda, H. G., Zabel, F., Fink, E. H. and Becker, K. H.: J. Phys. Chem. 94, 5860, 1990.

IV.A2.237

C(O)FCl + hν → products

Primary photochemical processes

Reaction			$\Delta H°$/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
C(O)FCl + hν	→ FCO + Cl	(1)	396	302
	→ ClCO + F	(2)	485	247
	→ CO + F + Cl	(3)	517	231
	→ CFCl + O(^{3}P)	(4)	707	169

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi_1 + \Phi_3 = 0.98 \pm 0.09$	193	Hermann et al., 1994	(a,b,c)
$\Phi_1 + \Phi_3 = 0.90 \pm 0.05$	210 ± 2.5	Nölle et al., 1999	(a,d,e)
$\Phi_1 + \Phi_3 = 0.85 \pm 0.25$	210		(a,b,e)
$\Phi_1 + \Phi_3 = 0.77 \pm 0.33$	225.5		(a,b,e)
$\Phi_1 + \Phi_3 = 0.71 \pm 0.30$	230		(a,b,e)
$\Phi_1 + \Phi_3 = 0.52 \pm 0.14$	248		(a,b,e)

Comments

(a) The measured quantum yield is for the loss of C(O)FCl. The observed products were C(O)F_2 (and in the study of Hermann et al. (1994), also CO). Product formation was explained using only channels (1) and (3), because decomposition of ClCO formed in channel (2) makes channel (2) equivalent to channel (3). Formation of C(O)F_2 arises from the self-reaction of FCO radicals formed in channel (1), FCO + FCO → C(O)F_2 + CO. Channel (3) should not be accessible for wavelengths $>$ 231 nm, and hence the quantum yield measured by Nölle et al. (1999) at 248 nm is expected to be that for channel (1).

(b) Laser photolysis at 298 K.

(c) The initial C(O)FCl pressure was in the range 7–11 mbar. In addition to experiments in the absence of diluent gas, experiments were carried out with added N_2 diluent gas at total pressures of 100 and 900 mbar. The relative contribution of channels (1) and (3) depended on pressure with an equal contribution of the two channels at 900 mbar N_2.

(d) Photolysis with a medium pressure mercury lamp-monochromator combination at 298 K.

(e) The initial C(O)FCl pressure was $\sim$ 5 mbar, with no added diluent gas.

Preferred Values

Absorption cross-sections for C(O)FCl at 298 K

λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\sigma/\mathrm{cm}^2$
186.0	15.6	207.3	10.8
187.8	14.0	209.4	9.9
189.6	13.4	211.6	9.0
191.4	12.9	213.9	7.9
193.2	12.7	216.2	6.9
195.1	12.5	218.6	5.8
197.0	12.4	221.0	4.8
199.0	12.3	223.5	3.8
201.0	12.5	226.0	2.9
203.0	12.0	228.6	2.2
205.1	11.5	231.2	1.6

Quantum yields for C(O)FCl photolysis at 298 K

See Comments on Preferred Values

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Chou et al. (1977) over the wavelength range 186 to 199 nm and those reported by Nölle et al. (1993) at longer wavelengths. The spectrum shows little structure; the values listed are averages over 500 cm^{-1} intervals. Nölle et al. (1993) reported values over the wavelength range 200–260 nm and the temperature range 298–223 K. Their room temperature values are in good agreement with those of Chou et al. (1977). The effect of temperature on calculated photodissociation rates is negligible because no strong temperature dependence is observed in the atmospheric window region where photolysis occurs (190–230 nm). Hermann et al. (1994) and Nölle et al. (1999) photolyzed C(O)FCl at a number of specific wavelengths in the range 193–248 nm. Within the substantial measurement uncertainties, the overall quantum yield for loss of C(O)FCl decreases approximately linearly with wavelength from 1.0 at 193 nm to 0.5 at 248 nm. Until confirmatory data are available, use of the quantum yields measured by Hermann et al. (1994) and Nölle et al. (1999) is recommended. Pulsed laser photolysis at 235 nm of C(O)FCl in a supersonic jet coupled to time-of-flight spectroscopy showed that channel (1) is operative at this wavelength (Maul et al., 1999), and a value of ΔH^0(C(O)FCl)[0 K] = -(397 ± 15) kJ mol^{-1} was obtained.

References

Chou, C. G., Crescentini, G., Vera-Ruiz, H., Smith, W. S. and Rowland, F.S.: Results presented at the 173rd American Chemical Society National Meeting, New Orleans, March, 1977.
Hermann, M., Nölle, A. and Heydtmann, H.: Chem. Phys. Lett., 226, 559, 1994.
Maul, C., Dietrich, C., Haas, T. and Gericke, K.-H.: Phys. Chem. Chem. Phys., 1, 1441, 1999.
Nölle, A., Heydtmann, H., Meller, R. and Moortgat, G. K.: Geophys. Res. Lett., 20, 707, 1993.
Nölle, A., Krumscheid, C. and Heydtmann, H.: Chem. Phys. Lett., 299, 561, 1999.

IV.A2.238

$C(O)Cl_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction			$\Delta H°$/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$C(O)Cl_2 + h\nu$	$\rightarrow ClCO + Cl$	(1)	320	374
	$\rightarrow CO + 2Cl$	(2)	352	340
	$\rightarrow CCl_2 + O(^3P)$	(3)	699	171

Preferred Values

Absorption cross-sections for $C(O)Cl_2$ at 298 K

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
184.4	234	211.6	13.3
186.0	186	213.9	12.6
187.8	146	216.2	12.3
189.6	116	218.6	12.2
191.4	90.3	221.0	12.2
193.2	71.5	223.5	12.4
195.1	52.4	226.0	12.7
197.0	39.9	228.6	13.1
199.0	31.2	231.2	13.4
201.0	25.2	233.9	13.6
203.0	20.9	236.7	13.1
205.1	17.9	239.5	12.5
207.3	15.8	242.4	11.6
209.4	14.3		

Quantum yield for $C(O)Cl_2$ at 298 K

$\Phi(1) = 1.0$ for $\lambda > 184$ nm.

Comments on Preferred Values

The preferred values of the absorption cross sections are those reported by Gillotay et al. (1993). The spectrum is a continuum; the values listed are averaged over 500 cm^{-1} intervals. The results of Gillotay et al. (1993) are in good agreement with the earlier results of Chou et al. (1977). Gillotay et al. (1993) reported values over the wavelength range 170–310 nm and the temperature range 210–295 K. The temperature effect is only significant at longer wavelengths ($\lambda > 250$ nm). The observations of Wijnen (1961), Heicklen (1965) and earlier investigators (Calvert and Pitts, 1966) show that process (1) is the primary photolysis pathway. In the atmosphere, the overall photolysis proceeds by process (2) [i.e., ClCO decomposes to yield a second Cl atom] and the quantum yield for Cl atom formation will be 2.0.

References

Calvert, J. G. and Pitts, Jr., J. N.: ”Photochemistry,” page 231, John Wiley and Sons, Inc., New York, 1966.
Chou, G. C., Crescentini, G., Vera-Ruiz, H., Smith, W. S. and Rowland, F. S.: Results presented at the 173rd American Chemical Society National Meeting, New Orleans, March, 1977.
Gillotay, D., Simon, P. C. and Dierickx, L.: Aeronomica Acta, A368, 1993; Institut d’Aeronomie Spatiale de Belgique, Brussels, Belgium; presented at Quadrennial Ozone Symposium, Charlottesville, Virginia, June 1992.
Heicklen, J.: J. Am. Chem. Soc., 87, 445, 1965.
Wijnen, W. H.: J. Am. Chem. Soc., 83, 3014, 1961.

IV.A2.239

$CF_2ClCHO + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CF_2ClCHO + h\nu$	$\rightarrow CF_2Cl + HCO$	(1)		
	$\rightarrow CF_2ClCO + H$	(2)		
	$\rightarrow CHF_2Cl + CO$	(3)		

Absorption cross-section data

Wavelength range/nm	References	Comments
235-370	Rattigan et al., 1998	(a)

Quantum yield data

There are no reported quantum yield data.

Comments

(a) Absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 243–298 K. The UV spectrum of difluorochloroacetaldehyde shows a broad band, centered at 300 nm and extending out to 365 nm. Values of σ were given at 5 nm intervals at 298 K together with values of B in the expression ln $\sigma(T)$ = ln σ(298 K) + B(T-298).

Preferred Values

Absorption cross-sections for CF_2ClCHO at 298 K and their temperature dependence

Wavelength	$10^{20}\ \sigma$(298 K)/cm^2	10^4 B/K$^{-1 a)}$
235	0.192	-29.0
240	0.408	-17.9
245	0.736	-13.5
250	1.25	-11.8
255	1.99	-10.7
260	3.02	-10.5
265	4.36	-10.4
270	6.05	-10.5
275	8.00	-9.96
280	10.1	-10.6
285	12.1	-10.2
290	14.0	-10.6
295	15.4	-9.54
300	16.3	-10.4
305	15.9	-7.09
310	15.4	-9.73
315	13.4	-8.32

Wavelength	10^{20} σ(298 K)/cm^2	10^4 B/K^{-1}(a)
320	11.7	-7.71
325	9.24	-5.02
330	6.51	-3.03
335	4.76	-2.83
340	2.84	-2.84
345	1.52	14.0
350	0.711	37.3
355	0.148	68.1
360	0.036	75.8
365	0.012	52.9
370	0.003	63.1

(a) $\ln \sigma(T) = \ln \sigma(298\text{ K}) + B(T-298)$

Quantum yield for CF_2ClCHO

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are those reported by Rattigan et al. (1998). There are no data on the quantum yields but, by analogy with acetaldehyde which shows a similar absorption spectrum, photodissociation is expected to be predominantly by channel (1).

References

Rattigan, O. V., Wild, O. and Cox, R. A.: J. Photochem. Photobiol. A: Chem., 112, 1, 1998.

IV.A2.240

$CFCl_2CHO + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CFCl_2CHO + h\nu$	$\rightarrow CFCl_2 + HCO$	(1)		
	$\rightarrow CFCl_2CO + H$	(2)		
	$\rightarrow CHFCl_2 + CO$	(3)		

Absorption cross-section data

Wavelength range/nm	References	Comments
235-370	Rattigan et al., 1998	(a)

Quantum yield data

There are no reported quantum yield data.

Comments

(a) Absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 243–298 K. The UV spectrum of difluorochloroacetaldehyde shows a broad band, centered at 300 nm and extending out to 365 nm. Values of σ were given at 5 nm intervals at 298 K together with values of B in the expression $\ln \sigma(T) = \ln \sigma(298\ K) + B(T\text{-}298)$.

Preferred Values

Absorption cross-sections for $CFCl_2CHO$ at 298 K and their temperature dependence

Wavelength	$10^{20}\ \sigma$(298 K)/cm^2	10^4 B/K^{-1}(a)
235	0.402	136.0
240	0.502	87.0
245	1.080	30.6
250	1.597	6.41
255	2.391	1.24
260	3.483	-6.12
265	4.869	-7.55
270	6.527	-8.11
275	8.351	-8.28
280	10.1	-8.04
285	11.8	-7.82
290	13.0	-6.89
295	13.7	-6.41

Wavelength	10^{20} σ(298 K)/cm^2	10^4 B/K^{-1}(a)
300	13.6	-4.50
305	12.9	-2.93
310	11.6	1.73
315	9.80	2.70
320	7.93	6.97
325	5.61	12.2
330	3.89	15.6
335	2.46	24.6
340	1.26	36.5
345	0.628	58.1
350	0.254	84.9
355	0.052	92.8
360	0.017	93.2
365	0.007	103.2
370	0.002	138.3

(a) $\ln \sigma(T) = \ln \sigma(298\text{ K}) + B(T\text{-}298)$

Quantum yield for $CFCl_2CHO$

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are those reported by Rattigan et al. (1998). There are no data on the quantum yields but, by analogy with acetaldehyde which shows a similar absorption spectrum, photodissociation is expected to be predominantly by channel (1).

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$CCl_3CHO + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CCl_3CHO + h\nu$	$\rightarrow CCl_3 + HCO$	(1)		
	$\rightarrow CCl_3CO + H$	(2)		
	$\rightarrow CHCl_3 + CO$	(3)		
	$\rightarrow CCl_2CHO + Cl$	(4)		

Absorption cross-section data

Wavelength range/nm	References	Comments
200-340	Rattigan et al., 1993	(a)
200-370	Rattigan et al., 1998	(b)
200-345	Talukdar et al., 2001	(c)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi[H] = 0.04 \pm 0.005$	193	Talukdar et al., 2001	(d)
$\Phi[O(^3P)] < 0.02$	248		
$\Phi[H] < 0.01$	248		
$\Phi[O(^3P)] < 0.01$	308		
$\Phi[H] < 0.002$	308		
$\Phi[Cl] = 1.3 \pm 0.3$	308		
$\Phi[-CCl_3CHO] = 1.00 \pm 0.05$	290-400	Wenger et al., 2004	(e)

Comments

(a) Absolute absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 240–300 K. The UV spectrum of trichloroacetaldehyde shows a broad band, centered at 290 nm and extending out to 360 nm. Values of σ were given at 5 nm intervals at 296 K and 243 K. A second absorption band appears at <230 nm.

(b) Absolute absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 243–298 K. Values of σ were given at 5 nm intervals at 298 K together with the values of B in the expression $\ln \sigma(T) = \ln \sigma(298\ K) + B(T\text{-}298)$.

(c) Absolute absorption cross-sections were measured using a diode array spectrometer over the temperature range 240–360 K. Values of σ were listed at 298 K at 2 nm intervals, together with the values of B in the expression $\ln \sigma(T) = \ln \sigma(298\ K) + B(T\text{-}298)$.

(d) Determined from pulsed laser photolysis of CCl_3CHO with detection of H, $O(^3P)$ and Cl atoms by resonance fluorescence. Experiments were carried out at 298 ± 2 K, and the H, $O(^3P)$ and Cl atom signals were placed on an absolute basis by use of photolysis of HBr (193 nm) or CH_3SH (248 and 308 nm) as reference compounds for H atom formation, photolysis of O_3 in the presence of N_2 at 248 and 308 nm as a reference compound for production of $O(^3P)$ atoms, and photolysis of Cl_2 at 308 nm as a reference compound for production of Cl atoms. Because Cl atoms react with CCl_3CHO, their yield was obtained by extrapolation to zero time. Cl atom formation was shown to be a primary process. Photolysis of CCl_3CHO at 248 nm in the presence of O_2 led to the formation of CO and $C(O)Cl_2$, with no formation of $CHCl_3$ (thereby ruling out the occurrence of channel (3) at 248 nm).

(e) Determined from the photolysis of CCl_3CHO in the ∼200 m^3 volume EUPHORE chamber under natural sunlight conditions at 298 ± 5 K. Cyclohexane was added to scavenge Cl atoms and SF_6 was added to monitor dilution and loss through leakage. CCl_3CHO was monitored by FTIR spectroscopy and GC. The formation yield of Cl atoms was obtained from the amounts of cyclohexane consumed during the photolyses. The measured decay rates of CCl_3CHO, corrected for dilution, were compared to the calculated decay rates for a photodissociation quantum yield of 1.00.

Preferred Values

Absorption cross-sections of CCl_3CHO at 298 K and their temperature dependence

Wavelength	10^{20} σ(298 K)/cm^2	10^4 B/K^{-1}(a)
200	186.9	22.0
202	152.5	23.9
204	121.8	27.2
206	95.7	30.6
208	73.8	34.1
210	56.3	37.5
212	42.6	40.9
214	31.8	44.0
216	23.8	47.2
218	17.7	50.2
220	13.1	52.9
222	9.75	55.6
224	7.24	57.6
226	5.39	59.0
228	4.06	60.4
230	3.07	60.5
232	2.39	59.5
234	1.90	55.9
236	1.62	49.2
238	1.43	41.6
240	1.39	33.0
242	1.41	24.0
244	1.53	16.4
246	1.66	10.4
248	1.91	6.50
250	2.18	3.73
252	2.54	1.50
254	2.92	0.324
256	3.36	-0.569
258	3.84	-0.877
260	4.35	-1.23
262	4.90	-1.65
264	5.48	-1.62
266	6.07	-1.50
268	6.68	-1.41
270	7.28	-1.22
272	7.88	-1.07
274	8.46	-0.931
276	8.99	-0.584
278	9.49	-0.412
280	9.94	-0.481
282	10.3	-0.235
284	10.6	0.242
286	10.8	0.475
288	10.9	0.750
290	10.9	1.09
292	10.8	1.51
294	10.6	1.96
296	10.3	2.38
298	9.92	2.71

Wavelength	10^{20} σ(298 K)/cm^2	10^4 B/K^{-1}(a)
300	9.25	3.07
302	8.77	3.60
304	8.17	4.37
306	7.50	5.25
308	6.86	6.10
310	6.18	6.91
312	5.58	7.90
314	4.98	9.30
316	4.33	11.2
318	3.68	13.2
320	3.09	15.1
322	2.51	16.7
324	2.09	18.5
326	1.76	21.1
328	1.43	25.0
330	1.12	30.3
332	0.849	36.6
334	0.590	43.3
336	0.373	49.8
338	0.261	55.6
340	0.188	60.2
342	0.136	65.0
344	0.100	69.0

(a) $\ln \sigma(T) = \ln \sigma(298\ \mathrm{K}) + \mathrm{B}(T\text{-}298)$

Quantum yield for CCl_3CHO

$\Phi(4) = 1.0$ over the wavelength range 290–400 nm.

Comments on Preferred Values

The preferred values for the cross-sections are those reported by Talukdar et al. (2001), which are in excellent agreement with the earlier data of Rattigan et al. (1998) except at 230–250 nm where the Rattigan et al. (1998) cross-sections are somewhat lower. The preferred quantum yield is based on the studies of Talukdar et al. (2001) at 308 nm and of Wenger et al. (2004) using natural sunlight photolysis over the wavelength region 290–400 nm. Wenger et al. (2004) observed the formation of $C(O)Cl_2$, CO and Cl atoms from the photolysis of CCl_3CHO at 290–400 nm, with molar yields of 0.83 ± 0.04, 1.01 ± 0.05 and 1.18 ± 0.06, respectively, which when combined with the data of Talukdar et al. (2001) indicates that the dominant primary process at $\lambda > 290$ nm is to form Cl + CCl_2CHO [channel (4)].

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$CF_3C(O)Cl + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CF_3C(O)Cl + h\nu$	$\rightarrow CF_3 + ClCO$	(1)		
	$\rightarrow CF_3CO + Cl$	(2)		

Absorption cross-section data

Wavelength range/nm	References	Comments
200-330	Meller and Moortgat, 1997	(a)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi_1 + \Phi_2 = 0.95 \pm 0.05$	254	Meller and Moortgat, 1997	(b)
$\Phi_1 + \Phi_2 = 1.01 \pm 0.11$	193	Maricq and Szente, 1995	(c)
$\Phi_1 + \Phi_2 = 1.01 \pm 0.11$	248		
$\Phi_1 + \Phi_2 = 0.98 \pm 0.13$	254-280	Weibel et al., 1995	(d)

Comments

(a) Absolute absorption cross-sections were measured using a diode array spectrometer over the temperature range 223–298 K. The UV spectrum of trifluoroacetyl chloride shows two overlapping bands, the first having a maximum at 255 nm ($\sigma = 6.87 \times 10^{-19}$ cm^2 molecule^{-1}), and the second at $\lambda < 200$ nm. There is significant absorption at wavelengths > 300 nm, where the cross-sections become increasingly temperature dependent. The estimated overall errors in the values of σ were ± 3% over the wavelength range 200–310 nm, increasing to ± 20% for longer wavelengths where the cross-sections (and hence absorptions) are low. Values of σ were presented at 2 nm intervals at 223 K, 248 K, 273 K and 298 K. The measured absorption cross-sections were fit to the equation $\ln\sigma(\lambda, T) = A_0 + A_1\lambda + A_2\lambda^2 + A_3\lambda^3 + A_4\lambda^4 + (B_0 + B_1\lambda + B_2\lambda^2 + B_3\lambda^3 + B_4\lambda^4)(T - 273)$, with the following values which fit the measurements to within 3% throughout most of the spectrum, but with larger errors in the range 220–230 nm (up to 6% error) and at >300 nm (up to 20% error at 330 nm):

	λ = 200-220 nm	λ = 218-330 nm
A_0	-2.0111750×10^{4}	-8.8912918×10^{1}
A_1	3.1757333×10^{2}	9.6418661×10^{-1}
A_2	-2.5671017	$-5.4370794 \times 10^{-3}$
A_3	7.8520098×10^{-3}	1.4975946×10^{-5}
A_4	$-8.9707718 \times 10^{-6}$	$-1.6768324 \times 10^{-7}$
B_0	3.0306320×10^{2}	3.7950580
B_1	-5.8082356	$-5.9114731 \times 10^{-2}$
B_2	4.1715164×10^{-2}	3.4406419×10^{-4}
B_3	$-1.3306565 \times 10^{-4}$	$-8.8699856 \times 10^{-7}$
B_4	1.5906451×10^{-7}	$8.5483894 \times 10^{-10}$

(b) Average of measurements of the overall loss of $CF_3C(O)Cl$ during photolysis in N_2. Measurements of the photodissociation quantum yield of $CF_3C(O)Cl$ in air at total pressures of 67–1013 mbar showed no effect of total pressure or of the presence of O_2.

(c) Pulsed laser photolysis of $CF_3C(O)Cl$-C_2H_6-O_2-N_2 mixtures at a total pressure of 160 mbar, with detection of CF_3O_2 radicals by time-resolved UV spectroscopy and of HCl by IR spectroscopy. CF_3O_2 radicals were formed from CF_3 radicals and HCl was formed from $Cl + C_2H_6 \rightarrow HCl + C_2H_5$. The system was calibrated by photolysis of CH_3Cl at 193 nm and of Cl_2 at 248 nm instead of $CF_3C(O)Cl$, with the assumption that the photodissociation quantum yields of CH_3Cl and Cl_2 are unity.

(d) Quantum yields derived from the amounts of C_2F_6 and CF_3Cl formed from irradiating $CF_3C(O)Cl$ at 254 and 280 nm (high pressure mercury arc-monochromator combination). Actinometry was performed with potassium ferrioxalate solution. It was observed that $(2[C_2F_6] + [CF_3Cl])/[CO] = 0.99 \pm 0.05$, consistent with formation of CF_3 radicals, Cl atoms and CO followed by the combination reactions $CF_3 + CF_3 \rightarrow C_2F_6$ and $CF_3 + Cl \rightarrow CF_3Cl$. Hence $\Phi(\text{-}CF_3Cl(O)Cl) = 2\Phi(C_2F_6) + \Phi(CF_3Cl)$.

Preferred Values

Absorption cross-sections of CF_3COCl at 298 K and their temperature dependence

λ/nm	$10^{20}\ \sigma/cm^2$ 298 K	$10^{20}\ \sigma/cm^2$ 223 K
200	50.16	45.83
202	30.47	26.56
204	17.70	14.63
206	9.960	7.830
208	5.567	4.197
210	3.274	2.461
212	2.102	1.662
214	1.620	1.361
216	1.442	1.343
218	1.484	1.421
220	1.665	1.641
222	1.896	1.845
224	2.201	2.184
226	2.544	2.538
228	2.904	2.901
230	3.278	3.261
232	3.685	3.646
234	4.080	4.025
236	4.505	4.456
238	4.902	4.852
240	5.283	5.223
242	5.629	5.553

λ/nm	10^{20} σ/cm^2 298 K	10^{20} σ/cm^2 223 K
244	5.957	5.900
246	6.271	6.177
248	6.503	6.411
250	6.694	6.577
252	6.799	6.679
254	6.863	6.712
256	6.858	6.674
258	6.786	6.586
260	6.599	6.383
262	6.393	6.148
264	6.159	5.875
266	5.859	5.567
268	5.510	5.219
270	5.120	4.814
272	4.726	4.396
274	4.306	3.965
276	3.876	3.564
278	3.444	3.133
280	3.035	2.724
282	2.630	2.304
284	2.253	1.931
286	1.907	1.619
288	1.593	1.334
290	1.324	1.090
292	1.082	0.8672
294	0.8670	0.6739
296	0.6811	0.5117
298	0.5282	0.3977
300	0.4038	0.2978
302	0.3035	0.2178
304	0.2214	0.1520
306	0.1580	0.1018
308	0.1087	0.0642
310	0.0722	0.0376
312	0.0472	0.0211
314	0.0301	0.0115
316	0.0189	0.0061
318	0.0123	0.0033
320	0.0084	0.0019
322	0.0057	
324	0.0037	
326	0.0025	
328	0.0017	

Quantum yield for CF_3COCl

$\Phi_1 + \Phi_2 = 1.0$ over the wavelength range 200–325 nm.

Comments on Preferred Values

The data of Meller and Moortgat (1997) are in good agreement with the earlier results of Rattigan et al. (1993) and Jemi-Alade et al. (1991), except in the region of minimum absorption near 220 nm. The preferred values for the cross-sections are those reported by Meller and Moortgat (1997). The quantum yield is based on the measurements of Meller and Moortgat (1997), Marciq and Szente (1995) and Weibel et al. (1995). Maricq and Szente (1995) concluded that at 193 and 248 nm photolysis proceeds via channel (1), with the CF_3CO radical dissociating totally at 193 nm and $\sim$ 86% of the time at 248 nm. This interpretation (Maricq and Szente, 1995) is reasonably consistent with the product data of Weibel et al. (1995) for the wavelength range 254–280 nm and of Malanca et al. (1997, 1998) at 254 nm.

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Appendix 3: BrO_x Reactions

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$$HO + CH_3Br \rightarrow H_2O + CH_2Br$$

ΔH° = -71.9 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.8) \times 10^{-14}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
7.93×10^{-13} exp[-(889 ± 59)/T]	244-350	Davis et al., 1976	FP-RF
$(4.14 \pm 0.43) \times 10^{-14}$	298		
2.35×10^{-12} exp[-(1300 ± 150)/T]	233-379	Mellouki et al., 1992	PLP-LIF
$(2.96 \pm 0.36) \times 10^{-14}$	298		
5.79×10^{-12} exp[-(1560 ± 150)/T]	250-400	Zhang et al., 1992	FP-RF
$(3.08 \pm 0.47) \times 10^{-14}$	298		
1.86×10^{-12} exp[-(1230 ± 150)/T]	248-390	Chichinin et al., 1994	DF-EPR
$(3.03 \pm 0.45) \times 10^{-14}$	298		
Relative Rate Coefficients			
5.43×10^{-18} T^2 exp[-(812 ± 46)/T]	298-360	Hsu and Demore, 1994	RR (a)
3.16×10^{-14}	298		

Comments

(a) HO radicals were generated from the UV photolysis of O_3 in the presence of water vapor, in O_3-H_2O-CH_3Br-CH_3CHF_2-O_2-N_2 mixtures. The concentrations of CH_3Br and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CH_3Br)/k(HO + CH_3CHF_2) = (1.94 \pm 0.28)$ exp[-(232 ± 46)/T] is placed on an absolute basis by use of a rate coefficient of $k(HO + CH_3CHF_2) = 2.80 \times 10^{-18}$ T^2 exp(-580/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 2.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.7 \times 10^{-12}$ exp(-1215/T) cm^3 molecule^{-1} s^{-1} over the temperature range 240-300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta (E/R) = \pm 150$ K.

Comments on Preferred Values

The recent absolute rate coefficient measurements of Mellouki et al. (1992), Zhang et al. (1992) and Chichinin et al. (1994), which are in excellent agreement, are significantly lower than those previously determined by Howard and Evenson (1976) and Davis et al. (1976). The relative rate coefficients of Hsu and DeMore (1994) are also in excellent agreement with the absolute rate coefficients of Mellouki et al. (1992), Zhang et al. (1992) and Chichinin et al. (1994). A unit-weighted least-squares analysis of the rate coefficients of Mellouki et al. (1992), Zhang et al. (1992) and Chichinin et al. (1992), using the three parameter expression $k = CT^2$ exp(-D/T), leads to k = 3.44 × 10^{-18} T^2 exp(-687 /T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 233–400 K. The preferred Arrhenius expression, $k = A$ exp(-B/T), is centered on a mid-range temperature, T_m, of 265 K and is derived from three parameter expression with $A = C\ e^2\ T_m^2$ and $B = D + 2T_m$.

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$$\mathbf{HO + CH_2Br_2 \rightarrow H_2O + CHBr_2}$$

ΔH° = -79.6 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.91×10^{-12} exp[-(840 ± 100)/T]	243-380	Mellouki et al., 1992	PLP-LIF
(1.13 ± 0.15) × 10^{-13}	298		
1.51×10^{-12} exp[-(720 ± 60)/T]	288-368	Zhang et al., 1997	DF-RF
(1.33 ± 0.14) × 10^{-13}			
Relative Rate Coefficients			
(9.7 ± 0.6) × 10^{-14}	298	Orlando et al., 1996	RR (a)
1.51×10^{-12} exp[-(715 ± 39)/T]	293-375	DeMore, 1996	RR (b)
1.37×10^{-13}	298		

Comments

(a) HO radicals were generated by the photolysis of O_3 in the presence of H_2O, and acetone was used as the reference compound. CH_2Br_2 and acetone were monitored by FTIR spectroscopy, and a rate coefficient ratio of k(HO + CH_2Br_2)/k(HO + acetone) = 0.54 ± 0.03 was determined. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(HO + acetone) = 1.8×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of H_2O, and CH_2Cl_2 was used as the reference compound. CH_2Br_2 and CH_2Cl_2 were monitored by FTIR spectroscopy, and a rate coefficient ratio of k(HO + CH_2Br_2)/k(HO + CH_2Cl_2) = 0.84 exp[(145 ± 39)/T] was determined. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(HO + CH_2Cl_2) = 1.8×10^{-12} exp(-860/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.5 \times 10^{-12}$ exp(-775/T) cm^3 molecule^{-1} s^{-1} over the temperature range 240-300 K.

Reliability

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

Comments on Preferred Values

The room temperature rate coefficients of Mellouki et al. (1992), Orlando et al. (1996), DeMore (1996) and Zhang et al. (1997) range from 9.7×10^{-14} cm^3 molecule^{-1} s^{-1} to 1.43×10^{-13} cm^3 molecule^{-1} s^{-1}. The relative rate coefficients of DeMore (1996) and the absolute rate coefficients of Zhang et al. (1997), obtained over the temperature range ∼290–370 K, are systematically higher than the absolute rate data of Mellouki et al. (1992), by ∼20% at 290 K and ∼10% at 370 K. Because the Mellouki et al. (1992) study included measurements down to significantly lower temperatures than did the other studies, and their room temperature rate coefficient is in between those of Orlando et al. (1996), DeMore (1996) and Zhang et al. (1997), the Mellouki et al. (1992) study is used as the basis for the preferred values. While an Arrhenius plot of the Mellouki et al. (1992) data shows little evidence for curvature, the absolute rate coefficients of Mellouki et al. (1992) have been fitted to the three-parameter expression $k = CT^2 \exp(-D/T)$, resulting in k = 2.86 × 10^{-18} T^2 exp(-246/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 243–380 K. The preferred Arrhenius expression, $k = A \exp(B/T)$, is centered on a mid-range temperature, T_m, of 265 K and is derived from three parameter expression with $A = C\ e^2\ T_m^2$ and $B = D + 2T_m$.

References

DeMore, W. B.: J. Phys. Chem., 100, 5813, 1996.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Mellouki, A., Talukdar, R. K., Schmoltner, A.-M., Gierczak, T., Mills, M. J., Solomon, S. and Ravishankara, A. R.: Geophys. Res. Lett., 19, 2059, 1992.
Orlando, J. J., Tyndall, G. S., Wallington, T. J. and Dill, M.: Int. J. Chem. Kinet., 28, 433, 1996.
Zhang, Z., Zhong, J. and Qiu, L.: J. Atmos. Chem., 27, 209, 1997.

IV.A3.245

$HO + CHF_2Br \rightarrow H_2O + CF_2Br$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.4 \times 10^{-13} \exp[-(1050 \pm 400)/T]$	275-420	Brown et al., 1990	DF-RF
$(1.3 \pm 0.3) \times 10^{-14}$	298		
$7.4 \times 10^{-13} \exp[-(1300 \pm 100)/T]$	233-432	Talukdar et al., 1991	PLP-LIF/DF-LMR
$(1.06 \pm 0.08) \times 10^{-14}$	298		
$9.3 \times 10^{-13} \exp[-(1326 \pm 33)/T]$	298-460	Orkin and Khamaganov, 1993	DF-EPR
$(1.10 \pm 0.09) \times 10^{-14}$	298		
Relative Rate Coefficients			
$6.11 \times 10^{-21}\ T^{2.82} \exp[-(527 \pm 31)/T]$	283-368	Hsu and DeMore, 1995	RR (a)
9.9×10^{-15}	298		

Comments

(a) HO radicals were generated by the UV photolysis of O_3 in the presence of water vapor in O_3-H_2O-CHF_2Br-CH_4-O_2-N_2 mixtures. The concentrations of CHF_2Br and CH_4 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + CHF_2Br)/k(HO + CH_4) = (0.33 \pm 0.03) \exp[(460 \pm 31)/T]$ is placed on an absolute basis by using a rate coefficient of $k(HO + CH_4) = 1.85 \times 10^{-20}\ T^{2.82} \exp(-987/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.9 \times 10^{-13} \exp(-1300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-360 K.

Reliability

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

Comments on Preferred Values

The absolute coefficients of Talukdar et al. (1991) and Orkin and Khamaganov (1993), and the relative rate data of Hsu and DeMore (1995) are in excellent agreement at 298 K. The absolute rate coefficients of Brown et al. (1990) are significantly higher and are not used in the evaluation. Above room temperature, the absolute rate coefficients of Talukdar et al. (1991) are lower than those of Orkin and Khamaganov (1993): at 430 K the rate coefficient of Talukdar et al. (1991) is 20% lower than that of Orkin and Khamaganov (1993). The data of Hsu and DeMore (1995) display a slightly higher temperature dependence than those observed in the absolute rate studies at temperatures up to 370 K.

The preferred 298 K rate coefficient is the mean of the absolute rate coefficients of Talukdar et al. (1991), Orkin and Khamaganov (1993) and the relative rate coefficient Hsu and DeMore (1995). The temperature dependence is that measured by Talukdar et al. (1991), with the pre-exponential factor adjusted to fit the 298 K preferred value.

References

Brown, A. C., Canosa-Mas, C. E., Parr, A. D., Rothwell, K. and Wayne, R. P.: Nature 347, 541, 1990.
Hsu, K.-J. and DeMore, W. B.: J. Phys. Chem. 99, 1235, 1995.
IUPAC: http://www.iupac-kinetic.ch.cam.ac.uk/, 2007.
Orkin, V. L. and Khamaganov, V. G.: J. Atmos. Chem. 16, 169, 1993.
Talukdar, R., Mellouki, A., Gierczak, T., Burkholder, J. B., McKeen, S. A. and Ravishankara, A. R.: Science 252, 693, 1991.

IV.A3.246

HO + CF_3Br → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<1.2 \times 10^{-16}$	298	Burkholder et al., 1991	DF-LMR/PLP-LIF
$<2.0 \times 10^{-17}$	298	Orkin and Khamaganov, 1993	DF-EPR
$<4.0 \times 10^{-16}$	460		

Preferred Values

$k < 6.0 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k < 1.0 \times 10^{-12}$ exp(-3600/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250-460 K.

Comments on Preferred Values

Only upper limits to the rate coefficients were observed in the studies of Burkholder et al. (1991) and Orkin and Khamaganov (1993). The A-factor for the reaction was estimated to be $\sim 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The lower limit for E/R was estimated to be >3600 K based on the upper limit value of the rate coefficient determined by Orkin and Khamaganov (1993) at 460 K. The upper limit for the rate coefficient at 298 K is obtained using these parameters.

References

Burkholder, J. B., Wilson, R. R., Gierczak, T., Talukdar, R., McKeen, S. A., Orlando, J. J., Vaghjiani, G. L. and Ravishankara, A. R.: J. Geophys. Res. 96, 5025, 1991.
Orkin, V. L. and Khamaganov, V. G.: J. Atmos. Chem. 16, 169, 1993.

IV.A3.247

HO + $CF_2ClBr \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<1 \times 10^{-15}$	293	Clyne and Holt, 1979	DF-RF
$<2 \times 10^{-16}$	293	Burkholder et al., 1991	DF-LMR
$<9 \times 10^{-17}$	297		PLP-LIF
$<7 \times 10^{-17}$	373		PLP-LIF
$<2 \times 10^{-16}$	424		DF-LMR

Preferred Values

$k < 1 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k < 1 \times 10^{-12}$ exp(-3450/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250-380 K.

Comments on Preferred Values

The studies of Clyne and Holt (1979) and Burkholder et al. (1991) both observed no reaction of HO radicals with CF_2ClBr. The preferred upper limit Arrhenius expression is obtained from an assumed Arrhenius pre-exponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} and the upper limit rate coefficient at 373 K measured by Burkholder et al. (1991). The resulting upper limit Arrhenius expression yields a 298 K upper limit rate coefficient which is consistent with the room temperature data of Clyne and Holt (1979) and Burkholder et al. (1991).

References

Burkholder, J. B., Wilson, R. R., Gierczak, T., Talukdar, R., McKeen, S. A., Orlando, J. J., Vaghjiani, G. L. and Ravishankara, A. R.: J. Geophys. Res., 96, 5025, 1991.
Clyne, M. A. A. and Holt, P. M.: J. Chem. Soc. Faraday Trans. 2, 75, 569, 1979.

IV.A3.248

HO + $CF_2Br_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<4.0 \times 10^{-16}$	384-424	Burkholder et al., 1991	DF-LMR/PLP-LIF
$<5.0 \times 10^{-16}$	298		

Preferred Values

$k < 5.0 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k < 1.0 \times 10^{-12}$ exp(-2200/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250-460 K.

Comments on Preferred Values

The preferred upper limit is based on the sole study of Burkholder et al. (1991). The preferred upper limit to the rate coefficient at 298 K is confirmed by the values of $k < 4 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} measured at 384 and 424 K. The A-factor for the reaction was estimated to be $\sim 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The lower limit for E/R was estimated to be $>$ 2200 K based on the upper limit value of the rate coefficient determined by Burkholder et al. (1991) at 298 K.

References

Burkholder, J. B., Wilson, R. R., Gierczak, T., Talukdar, R., McKeen, S. A., Orlando, J. J., Vaghjiani, G. L. and Ravishankara, A. R.: J. Geophys. Res. 96, 5025, 1991.

IV.A3.249

$HO + CF_3CH_2Br \rightarrow H_2O + CF_3CHBr$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
8.5×10^{-13} exp[-(1113 ± 35)/T]	298-460	Orkin and Khamaganov, 1993	DF-EPR
(2.05 ± 0.16) × 10^{-14}	298		
1.39×10^{-12} exp[-(1350 ± 195)/T]	280-353	Nelson et al., 1993	DF-LIF
(1.45 ± 0.13) × 10^{-14}	294		

Preferred Values

$k = 1.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.4 \times 10^{-12} \exp(-1340/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280-460 K.

Reliability

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

Comments on Preferred Values

The rate coefficients of Nelson et al. (1993) are ∼15-25% lower than those of Orkin and Khamaganov (1993) over the temperature range common to both studies (298–353 K). A least-squares analysis of the rate coefficients of Orkin and Khamaganov (1993) and Nelson et al. (1993) yields the preferred Arrhenius expression.

References

Nelson Jr., D. D., Zahniser, M. S. and Kolb, C. E.: Geophys. Res. Lett. 20, 197, 1993.
Orkin, V. L. and Khamaganov, V. G.: J. Atmos. Chem. 16, 169, 1993.

IV.A3.250

$HO + CF_3CHFBr \rightarrow H_2O + CF_3CFBr$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.13 \times 10^{-12} \exp[-(1250 \pm 364)/T]$	279-423	Brown et al., 1990	DF-RF
$(1.7 \pm 0.3) \times 10^{-14}$	298		
$7.2 \times 10^{-13} \exp[-(1111 \pm 32)/T]$	298-460	Orkin and Khamaganov, 1993	DF-EPR
$(1.75 \pm 0.17) \times 10^{-14}$	298		

Preferred Values

$k = 1.7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.1 \times 10^{-13} \exp(-1155/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270-460 K.

Reliability

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

Comments on Preferred Values

The absolute rate coefficients of Brown et al. (1990) and Orkin and Khamaganov (1993) are in good agreement. A least-squares analysis of the rate coefficients of Brown et al. (1990) and Orkin and Khamaganov (1993) yields the preferred values.

References

Brown, A. C., Canosa-Mas, C. E., Parr, A. D., Rothwell, K. and Wayne, R. P.: Nature 347, 541, 1990.
Orkin, V. L. and Khamaganov, V. G.: J. Atmos. Chem. 16, 169, 1993.

IV.A3.251

$HO + CF_3CHClBr \rightarrow H_2O + CF_3CClBr$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.0 \pm 0.4) \times 10^{-14}$	303	Brown et al., 1989; 1990	DF-RF
$1.28 \times 10^{-12} \exp[-(995 \pm 38)/T]$	298-460	Orkin and Khamaganov, 1993	DF-EPR
$(4.50 \pm 0.40) \times 10^{-14}$	298		

Preferred Values

$k = 4.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.2 \times 10^{-12} \exp(-970/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290-460 K.

Reliability

$\Delta \log k = \pm 0.20$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The rate coefficient of Brown et al. (1989; 1990) at 303 K is ∼25% higher than that calculated from the Arrhenius expression of Orkin and Khamaganov (1993). A least-squares analysis of the rate coefficients of Orkin and Khamaganov (1993) leads to the preferred Arrhenius expression.

References

Brown, A. C., Canosa-Mas, C. E., Parr, A. D., Pierce, J. M. T. and Wayne, R. P.: Nature, 341, 635, 1989.
Brown, A. C., Canosa-Mas, C. E., Parr, A. D. and Wayne, R. P.: Atmos. Environ., 24A, 2499, 1990.
Orkin, V. L. and Khamaganov, V. G.: J. Atmos. Chem., 16, 169, 1993.

IV.A3.252

HO + $CF_2BrCF_2Br \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<1.5 \times 10^{-16}$	298	Burkholder et al., 1991	DF-LMR/PLP-LIF
$<2.0 \times 10^{-17}$	298	Orkin and Khamaganov, 1993	DF-EPR
$<4.0 \times 10^{-16}$	460		

Preferred Values

$k < 6 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k < 1 \times 10^{-12}$ exp(-3600/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250-460 K.

Comments on Preferred Values

Only upper limits to the rate coefficients were observed in the studies of Burkholder et al. (1991) and Orkin and Khamaganov (1993). The A-factor for the reaction was estimated to be $\sim 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The lower limit for E/R was estimated to be $>$ 3600 K based on the upper limit value of the rate coefficient determined by Orkin and Khamaganov (1993) at 460 K. The upper limit for the rate coefficient at 298 K is obtained using these parameters.

References

Burkholder, J. B., Wilson, R. R., Gierczak, T., Talukdar, R., McKeen, S. A., Orlando, J. J., Vaghjiani, G. L. and Ravishankara, A. R.: J. Geophys. Res. 96, 5025, 1991.
Orkin, V. L. and Khamaganov, V. G.: J. Atmos. Chem. 16, 169, 1993.

IV.A3.253

$$\mathbf{HO_2 + CH_2BrO_2 \rightarrow O_2 + CH_2BrO_2H \quad (1)}$$
$$\mathbf{\rightarrow O_2 + HC(O)Br + H_2O \quad (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.7 \pm 3.8) \times 10^{-12}$	298	Villenave and Lesclaux, 1995	FP-UVA (a)
Branching Ratios			
$k_1/k \geq 0.85$ $k_2/k \leq 0.15$	297	Chen et al., 1995	UVP-FTIR (b)

Comments

(a) Flash photolysis of Cl_2 in the presence of CH_3Br-CH_3OH-O_2-N_2 mixtures at a pressure of 1013 mbar. Decays in transient absorptions (with contributions from CH_2BrO_2 and HO_2) were recorded in the wavelength range 250 nm to 280 nm. k derived from simulations of the decay traces using an explicit reaction mechanism.

(b) CH_2BrO_2 and HO_2 radicals were generated from the steady-state photolysis of Cl_2 in the presence of CH_3Br-H_2-air mixtures at 933 mbar. FTIR spectroscopic analysis identified CH_2BrO_2H and HC(O)Br as carbon-containing primary products. The cited branching ratios were derived by taking account of secondary reactions in the system, and the possibility that HC(O)Br is formed from the in-situ oxidation of CH_2BrO_2H.

Preferred Values

$k = 6.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta (k_1/k) = {}^{+0.00}_{-0.15}$ at 298 K.

Comments on Preferred Values

While the above value of the rate coefficient seems reasonable, it has been derived from the analysis of a comparatively complex chemical system and requires independent verification to reduce the recommended error limits. Within the uncertainty of the determination (Villenave and Lesclaux, 1995), k is indistinguishable from that recommended for the reactions of HO_2 with CH_3O_2 and CH_2ClO_2 suggesting that, like Cl, the presence of the Br group has only a minor influence on the rate coefficient. However, the reported dominance of channel (1) (Chen et al., 1995) contrasts with that observed for CH_2ClO_2, for which formation of HC(O)Cl, H_2O and O_2 is the major pathway. Confirmatory product studies are also required.

References

Chen, J., Catoire, V. and Niki, H.: Chem. Phys. Lett. 245, 519, 1995.
Villenave, E. and Lesclaux, R.: Chem. Phys. Lett. 236, 376, 1995.

IV.A3.254/255

$$\mathbf{RO_2 + NO \rightarrow RO + NO_2} \qquad \mathbf{(1)}$$

$$\mathbf{RO_2 + NO + M \rightarrow RONO_2} \qquad \mathbf{(2)}$$

(254: R = CH_2Br; 255: R = $CHBr_2$)

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
R=CH_2Br			
$(1.07 \pm 0.11) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
R=$CHBr_2$			
$(1.74 \pm 0.16) \times 10^{-11}$	296	Bayes et al., 2005	PLP-RF (b)

Comments

(a) k determined from $+d[NO_2]/dt$ at a total pressure of 1 bar.

(b) Photolysis of $CHBr_3$ in the presence of O_2 and NO at 2.7–13 mbar. k was obtained from the formation kinetics of secondary Br atoms, generated from the prompt decomposition of $CHBr_2O$. k was independent of pressure in the studied range.

Preferred Values

R = CH_2Br
$k = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta\log k = \pm 0.3$ at 298 K.

R = $CHBr_2$
$k = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta\log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

R = CH_2Br
The preferred values are the rounded-off rate coefficients determined by Sehested et al. (1993).

R = $CHBr_2$
The preferred value is the rounded-off rate coefficient determined by Bayes et al. (2005).

References

Bayes, K. D., Friedl, R. R. and Sander S. P.: J. Phys. Chem., A 109, 3045, 2005.
Sehested, J., Nielsen, O. J. and Wallington, T. J.: Chem. Phys. Lett., 213, 157, 1993.

IV.A3.256

$$\begin{aligned} \mathbf{CH_2BrO_2 + CH_2BrO_2} &\rightarrow \mathbf{HC(O)Br + CH_2BrOH + O_2} \quad \mathbf{(1)} \\ &\rightarrow \mathbf{CH_2BrO + CH_2BrO + O_2} \quad \mathbf{(2)} \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_{obs} = (3.26 \pm 0.31) \times 10^{-11}$	298	Nielsen et al., 1991	PR-UVA (a,b)
$(1.05 \pm 0.40) \times 10^{-12}$	298	Villenave and Lesclaux, 1995	FP-UVA (c)
Branching Ratios			
$k_2/k \approx 1.0$	298	Nielsen et al., 1991	UVP-FTIR (d)
$k_2/k \approx 1.0$	297	Chen et al., 1995	UVP-FTIR (e)

Comments

(a) k_{obs} is based on the measured overall second-order decay of CH_2BrO_2, defined by $-d[CH_2BrO_2]/dt = 2k_{obs}[CH_2BrO_2]^2$. Br atoms and HO_2 radicals formed from the subsequent chemistry of CH_2BrO (formed from channel (2)) are expected to lead to secondary removal of CH_2BrO_2, such that k_{obs} represents an upper limit for the true value of k.

(b) Pulse radiolysis study of CH_3Br-O_2-SF_6 mixtures with CH_2BrO_2 radicals being monitored by UV absorption, with $\sigma_{250\ nm} = (7.20 \pm 0.83) \times 10^{-18}$ cm^2 molecule^{-1}. The derived value of k_{obs} was found to be independent of wavelength over the range 250–310 nm and of pressure over the range 150–1000 mbar of SF_6.

(c) Flash photolysis of Cl_2 in the presence of CH_3Br-O_2-N_2 mixtures at a pressure of 1013 mbar, with CH_2BrO_2 radicals being monitored by UV absorption, with $\sigma_{250\ nm} = (3.35 \pm 0.10) \times 10^{-18}$ cm^2 molecule^{-1}. Decays in transient absorption signals were recorded in the wavelength range 240 nm to 280 nm. k derived from simulations of the decay traces using an explicit reaction mechanism.

(d) CH_2BrO_2 radicals were generated from the steady-state photolysis of Cl_2 in the presence of CH_3Br–air mixtures. Two major carbon-containing products, CO and HC(O)Br, were observed by FTIR spectroscopic analysis. HC(O)Br was believed to arise from the reaction of CH_2BrO with O_2.

(e) CH_2BrO_2 radicals were generated from the steady-state photolysis of Cl_2 in the presence of CH_3Br-air mixtures at 930 mbar. FTIR spectroscopic analysis identified CH_2O as the major carbon-containing primary product, suggesting CH_2BrO (formed from channel (2)) predominantly decomposes by Br atom elimination. Lower yields of HC(O)Br were observed, but CH_2BrOH was not identified as a product. CO formation also observed from secondary reactions of primary products with Cl and Br.

Preferred Values

$k_2/k = 1.0$ at 298 K.

Reliability

$\Delta (k_2/k) = ^{+0.0}_{-0.1}$ at 298 K.

Comments on Preferred Values

The preferred unity value of k_2/k is based on the results of the product study of Chen et al. (1995), in which no evidence for formation of CH_2BrOH (which would be formed by channel (1)) was obtained. Observation of CH_2O as the major primary product was also consistent with the dominance of channel (2),followed by decomposition of CH_2BrO by Br atom elimination.

The two kinetics studies (Nielsen et al., 1991; Villenave and Lesclaux, 1995) are in significant disagreement, yielding rate coefficients which differ by more than an order of magnitude, and UV absorption spectra for CH_2BrO_2 which differ in both shape and magnitude. The spectrum reported by Villenave and Lesclaux (1995) is similar to that typically observed for peroxy radicals, with a single maximum at 240 nm. The spectrum reported by Nielsen et al. (1991) displays a second intense maximum at 280 nm, and thus appears to be subject to interference.

Although the value of k reported by Villenave and Lesclaux (1995) is likely to be indicative of the magnitude of the self-reaction rate coefficient for CH_2BrO_2, the mechanism used to extract k from the observed decay profiles assumed secondary removal of CH_2BrO_2 by reaction with HO_2 generated from the exclusive reaction of CH_2BrO with O_2. It is possible that the actual formation of Br atoms leads to a similar degree of secondary removal of CH_2BrO_2, but Villenave and Lesclaux (1995) did not observe formation of BrO (the likely product) in the system. More information is therefore needed on the kinetics and mechanism of the secondary reactions, in addition to further kinetics studies of the title reaction, to allow k to be defined more accurately.

References

Chen, J., Catoire, V. and Niki, H.: Chem. Phys. Lett. 245, 519, 1995.
Nielsen, O. J., Munk, J., Locke, G. and Wallington, T. J.: J. Phys. Chem. 95, 8714, 1991.
Villenave, E. and Lesclaux, R.: Chem. Phys. Lett. 236, 376, 1995.

IV.A3.257

$$\mathbf{BrCH_2CH_2O_2 + BrCH_2CH_2O_2 \rightarrow BrCH_2CH_2OH + BrCH_2CHO + O_2} \quad \textbf{(1)}$$
$$\mathbf{\rightarrow 2BrCH_2CH_2O + O_2} \quad \textbf{(2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
k_{obs}= $(6.2 \pm 1.2) \times 10^{-12}$	298	Crowley and Moortgat, 1992	MM-UVA (a,b)
$6.15 \times 10^{-14} \exp[(1247 \pm 203)/T]$	275-373	Villenave et al., 2003	FP-UVA (c)
$(4.49 \pm 0.22) \times 10^{-12}$	298		
Branching Ratios			
$k_1/k = 0.43$	296	Yarwood et al., 1992	UV-P-FTIR (d)
$k_2/k = 0.57$			

Comments

(a) k_{obs} is based on the measured overall second-order decay of $CH_2BrCH_2O_2$, defined by $-d[CH_2BrCH_2O_2]/dt = 2k_{obs}[CH_2BrCH_2O_2]^2$. As described in detail by Lesclaux (1997), HO_2 radicals formed from the subsequent chemistry of CH_2BrCH_2O (formed from channel (2)) are expected to lead to secondary removal of $CH_2BrCH_2O_2$. The true value of k is expected to fall in the range $k_{obs}/(1 + \alpha) < k < k_{obs}$, where $\alpha = k_2/k$.

(b) Molecular modulation study of the photolysis of Br_2 in the presence of C_2H_4-O_2-N_2 mixtures at total pressures up to 800 mbar. Modulated waveforms for the formation and removal of $CH_2BrCH_2O_2$ radicals were monitored by absorption at 270 nm, i.e. where HO_2 does not absorb.

(c) Flash photolysis of Br_2 in the presence of C_2H_4-O_2-N_2 mixtures at a pressure of 1013 mbar. Decays in transient absorption signals (with contributions from $CH_2BrCH_2O_2$ and HO_2) were recorded in the wavelength range 210 nm to 290 nm. k derived from simulations of the decay traces using an explicit reaction mechanism.

(d) Steady-state photolysis of Br_2 in the presence of C_2H_4-O_2-N_2 mixtures at 933 mbar total pressure, with FTIR spectroscopic determination of products. The major products observed were $BrCH_2CHO$, $BrCH_2CH_2OH$, and $BrCH_2CH_2OOH$. The branching ratio, $k_2/k_1 = 1.35 \pm 0.07$, was determined from the yields of $BrCH_2CHO$ and $BrCH_2CH_2OH$ relative to the loss of C_2H_4.

Preferred Values

$k = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.0 \times 10^{-14} \exp(1250/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270-380 K.
$k_1/k = 0.43$ at 298 K.
$k_2/k = 0.57$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 500$ K.
$\Delta (k_1/k) = (k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred values of k are based on the temperature dependence expression of Villenave et al. (2003), with which the earlier 298 K k_{obs} determination of Crowley and Moortgat (1992) is entirely consistent. The preferred values of the branching ratios are based on the data of Yarwood et al. (1992), which require confirmation.

The above value of k is similar to that for the self-reaction of $CH_2ClCH_2O_2$, both showing an enhancement of a factor of ca. 50 compared with the self-reaction rate coefficient for the unsubstituted analogue, $C_2H_5O_2$.

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$$
\begin{aligned}
\mathbf{BrO + CH_3O_2} \quad &\rightarrow \mathbf{CH_3O + BrOO} \quad &\mathbf{(1)}\\
&\rightarrow \mathbf{CH_3O + OBrO} \quad &\mathbf{(2)}\\
&\rightarrow \mathbf{HOBr + CH_2O_2} \quad &\mathbf{(3)}
\end{aligned}
$$

$\Delta H°(1)$ = -3.5 kJ·mol^{-1}
$\Delta H°(2)$= +52.4 kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.7 \pm 0.6) \times 10^{-12}$	298	Aranda et al., 1997	DF-MS/LIF (a)
Branching Ratios			
$k_3/k = 0.8 \pm 0.2$	298	Aranda et al., 1997	DF-MS/LIF (a)
$(k_1 + k_2)/k = 0.3 \pm 0.1$	298		

Comments

(a) Flow tube operated at 1.3 mbar of He. BrO and CH_3O_2 were formed in the reactions Br + O_3, and F + CH_4 in the presence of O_2, respectively, and monitored by MS as their parent ions. The experiments were conducted under pseudo first-order conditions, with BrO in excess of CH_3O_2. The products observed were HOBr (MS) and CH_3O (LIF). The CH_3O profile was modeled by taking into account its presence as impurity in the CH_3O_2 source, and its reaction with BrO.

Preferred Values

$k = 5.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.25$ at 298 K.
$k_3/k = 0.75$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (k_1/k) = \pm 0.2$ at 298 K.
$\Delta (k_3/k) = ^{+0.25}_{-0.4}$ at 298 K.

Comments on Preferred Values

The preferred value of k(298 K) is taken from the sole study of this reaction with expanded error limits. The branching ratio to HOBr formation (reaction 3) was determined as (0.8 ± 0.2), and that to CH_3O formation as (0.3 ± 0.1). Since this study, it has been shown that OBrO has a stable positive ion under similar experimental conditions (Li, 1999), and would have been observed by these authors if it were a significant product. They also report non-observation of CH_3OBr and HBr. We also note that channel (2) is significantly endothermic, whilst channel (3) is, within error limits, thermoneutral (Aranda et al., 1997). For this reason we do not consider reaction (2) and prefer to quote $k_1/k = 0.25$ and $k_3/k = 0.75$. We add expanded error limits to reflect the fact that calibration of the CH_3O signal was achieved by modeling the CH_3O_2 source chemistry, which contains significant uncertainty, and because HOBr was not directly calibrated. In the study of Aranda et al. (1997) it is not clear how the direct formation of HOBr in channel (3) was separated from the indirect formation via channel (1) followed by rapid reaction of CH_3O with the excess BrO (Aranda et al., 1998). Theoretical studies (Guha and Francisco, 2003) have been unable to reproduce the experimentally derived reaction mechanism and suggest that HOOBr and HCHO are formed via rearrangement of a CH_3OOOBr association complex. Further experiments to examine temperature dependent kinetics and product formation in this reaction are desirable.

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$CH_3Br + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		ΔH°/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CH_3Br + h\nu$	$\rightarrow CH_3 + Br$	296	404

Absorption cross-section data

Wavelength range/nm	Reference	Comments
180–260	Gillotay and Simon, 1988	(a)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
Φ(Br)=1.01 ± 0.16	248	Talukdar et al., 1992	(b)
Φ(Br)=1.10 ± 0.20	222		
Φ(Br)=1.05 ± 0.11	193		
Φ(H)=0.002 ± 0.001	193		

Comments

(a) Spectra were obtained using a thermostatted absorption cell with a single pass optical path of 2 m coupled to a monochromator capable of a maximum resolution of 0.015 nm. Pressures of CH_3Br used covered the range 0.053 - 29 mbar. Spectra were recorded at 295 K, 270 K, 250 K, 230 K and 210 K. The data were fitted to a polynomial expression giving the cross sections as a function of temperature and pressure.

(b) Pulsed laser photolysis of CH_3Br-N_2 or He mixtures and detection of $Br(^2P_{3/2})$ by resonance fluorescence. A small amount of H_2 was added to ensure rapid quenching of the $Br(^2P_{1/2})$ also produced. The $Br(^2P_{3/2})$ measurements were calibrated by HBr photolysis at 193 nm for which a quantum yield of unity was assumed. No H atom production could be detected in the 248 nm and 222 nm photolyses.

Preferred Values

Absorption cross-sections of CH_3Br at 295 K and 210 K.

λ/nm	$10^{20}\ \sigma$/cm^2 295 K	$10^{20}\ \sigma$/cm^2 210 K	λ/nm	$10^{20}\ \sigma$/cm^2 295 K	$10^{20}\ \sigma$/cm^2 210 K
190	43.9	(a)	226	23.0	21.6
192	52.9	(a)	228	18.8	17.7
194	62.0	(a)	230	15.4	14.4
196	69.1	(a)	232	12.4	11.4
198	76.0	(a)	234	9.87	8.86
200	79.1	(a)	236	7.65	6.58
202	79.7	(a)	238	5.95	4.97
204	79.3	(a)	240	4.47	3.79
206	76.7	(a)	242	3.35	2.76
208	72.7	(a)	244	2.50	1.94
210	66.6	(a)	246	1.82	1.42
212	61.4	61.3	248	1.31	0.980
214	55.9	55.6	250	0.957	0.675
216	49.3	49.0	252	0.686	0.447
218	44.2	43.3	254	0.487	0.315
220	37.7	36.6	256	0.336	0.202
222	32.4	31.2	258	0.235	0.129
224	27.6	25.9	260	0.164	0.088

(a) No detectable change in σ over the range 210–295 K

Quantum Yield

$\Phi = 1.0$ over the wavelength range 200–260 nm.

Comments on Preferred Values

The preferred values of the absorption cross-section at 295 K and 210 K are those reported by Gillotay and Simon (1988). Values have also been reported at 298 K by Molina et al. (1982) at 5 nm intervals and by Robbins (1976), at 2 nm intervals. The agreement among these three studies is very good. Gillotay and Simon (1988) have fitted their data to a polynomial to give an expression for the cross sections as a function of temperature and pressure.

The preferred values for the quantum yield are based on the study of Talukdar et al. (1992) who showed that photolysis occurs with unit quantum efficiency by rupture of the C-Br bond.

References

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IV.A3.260

$CF_3Br + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CF_3Br + h\nu$	$\rightarrow CF_3 + Br$	296	404

Absorption cross-section data

Wavelength range/nm	Reference	Comments
168–280	Gillotay and Simon, 1989	(a)
190-285	Burkholder et al., 1991	(b)
190-320	Orkin and Kasimovskaya, 1995	(c)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
1.12 ± 0.16	193	Talukdar et al., 1992	(d)
0.92 ± 0.15	222		

Comments

(a) Spectra were obtained using a thermostatted absorption cell with a single pass optical path of 2 m coupled to a monochromator capable of a maximum resolution of 0.015 nm. Pressures of CF_3Br used covered the range 0.8–950 mbar. Spectra were recorded at 295 K, 270 K, 250 K, 230 K and 210 K. The data were fitted to a polynomial expression giving the cross sections as a function of temperature and pressure.

(b) Spectra were obtained using thermostatted absorption cells with single pass optical paths of 98.1 cm and 150 cm, coupled to spectrographs having resolutions in the range 0.4–0.5 nm. Spectra were recorded at 296 K, 270 K, 250 K, 230 K and 210 K. The data werefitted to a polynomial expression giving the cross sections as a function of temperature and pressure.

(c) Spectra were obtained using a cell thermostatted at 295 K with a single path optical length of 14.0 cm and coupled to a double beam spectrophotometric system. Sample pressures in the range 0.013–1 bar were used.

(d) Pulsed laser photolysis of CF_3Br-N_2 mixtures and detection of $Br(^2P_{3/2})$ by resonance fluorescence. A small amount of H_2 was added to ensure rapid quenching of the $Br(^2P_{1/2})$ also produced. The $Br(^2P_{3/2})$ measurements were calibrated by CH_3Br photolysis at the same wavelength for which a quantum yield of unity was assumed.

Preferred Values

Absorption cross-sections of CF_3Br at 295 K and 210 K.

λ/nm	$10^{20}\ \sigma$/cm^2 295 K	$10^{20}\ \sigma$/cm^2 210 K	λ/nm	$10^{20}\ \sigma$/cm^2 295 K	$10^{20}\ \sigma$/cm^2 210 K
190	6.50	7.11	230	2.98	2.24
192	7.49	8.27	232	2.35	1.67
194	8.49	9.43	234	1.83	1.21
196	9.48	10.6	236	1.40	0.863
198	10.4	11.7	238	1.06	0.607
200	11.2	12.6	240	0.789	0.420
202	11.8	13.2	242	0.574	0.287
204	12.2	13.6	244	0.418	0.193
206	12.4	13.8	246	0.301	0.129
208	12.3	13.6	248	0.216	0.0848
210	12.0	12.9	250	0.153	0.0562
212	11.3	12.1	252	0.107	0.0371
214	10.6	11.1	254	0.0751	0.0241
216	9.69	9.86	256	0.0524	0.0163
218	8.65	8.54	258	0.0364	0.0110
220	7.58	7.25	260	0.0252	0.0074
222	6.52	5.97	262	0.0176	
224	5.50	4.84	264	0.0121	
226	4.56	3.86	266	0.0086	
228	3.73	2.96	268	0.0061	

Quantum Yields

$\Phi = 1.0$ over the wavelength range 200–270 nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K are the mean of the values obtained in the studies of Gillotay and Simon (1989), Burkholder et al. (1991) and Orkin and Kasimovskaya (1995). Molina et al. (1982) have also reported values at 5 nm intervals. The agreement among these four studies (Gillotay and Simon, 1989; Burkholder et al., 1991 and Orkin and Kasimovskaya, 1995) over the wavelength range of the preferred values is excellent. The temperature dependence of the of the cross sections down to 210 K has been studied by Gillotay and Simon (1989) and by Burkholder et al. (1991) and in both cases polynomial expressions were derived giving the cross sections as a function of temperature and wavelength. There are significant differences between the two studies (Gillotay and Simon, 1989; Burkholder et al., 1991). Thus at $\lambda > 220$ nm both studies reported a decrease in absorption as the temperature was lowered, but near the absorption peak ($\sim$ 205 nm) Burkholder et al. (1991) found the cross-sections to be independent of temperature, while Gillotay and Simon (1989) found the absorption to increase with decreasing temperature, with a 20% increase at the lowest temperature studied. Furthermore, at 210 K there is good agreement on the values of σ at longer wavelengths ($\sim$ 280 nm), but the discrepancy between the two studies (Gillotay and Simon, 1989; Burkholder et al., 1991) increases steadily in going to shorter wavelengths with the values of Gillotay and Simon (1989) being $\sim$30% larger than those of Burkholder et al. (1991) at 190 nm. Provisionally, the preferred values at 210 K are taken as the mean of the values of Gillotay and Simon (1989) and of Burkholder et al. (1991).

The preferred quantum yields are based on the study of Talukdar et al. (1992) in which it was shown that photolysis occurs with unit quantum efficiency by rupture of the C-Br bond to give CF_3 + Br. Studies of the dynamics of photodissociation at 234 nm show that 80% of the Br atoms are produced in the $^2P_{1/2}$ excited state (Kim et al., 2001). CF_3Br has no apparent tropospheric chemistry loss mechanism (Burkholder et al., 1991) and is estimated to have a tropospheric lifetime with respect to photolysis of greater than 1000 years (Molina et al., 1982).

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$CF_2ClBr + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			ΔH°/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CF_2ClBr + h\nu$	$\rightarrow CF_2 + ClBr$	(1)	296	445
	$\rightarrow CF_2Cl + Br$	(2)	271	441
	$\rightarrow CF_2Br + Cl$	(3)	348 (est)	344
	$\rightarrow CF_2 + Cl + Br$	(4)	488	245

Absorption cross-section data

Wavelength range/nm	Reference	Comments
170–302	Gillotay and Simon, 1989	(a)
190–320	Burkholder et al., 1991	(b)
190–304	Orkin and Kasimovskaya, 1995	(c)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\Phi(Cl) = 1.03 \pm 0.14$	193	Talukdar et al., 1996	(d)
$\Phi(Br) = 1.04 \pm 0.14$	193		
$\Phi(CF_2) = 0.9 \pm 0.2$	193		
$\Phi(Cl) = 0.27 \pm 0.04$	222		
$\Phi(Br) = 0.86 \pm 0.04$	222		
$\Phi(Cl) = 0.18 \pm 0.03$	248		
$\Phi(Br) = 0.75 \pm 0.12$	248		
$\Phi(3) = 0.29 \pm 0.03$	157.6	Yokoyama et al., 2001	(e)
$\Phi(2) = 0.46 \pm 0.05$	157.6		
$\Phi(4) = 0.25 \pm 0.05$	157.6		
$\Phi(3) = 0.24$	234	Lee and Yung, 2001	(f)
$\Phi(2) = 0.96$	234		

Comments

(a) Spectra were obtained using a thermostatted absorption cell with a single pass optical path of 2 m coupled to a monochromator capable of a maximum resolution of 0.015 nm. Pressures of CF_2ClBr used covered the range 0.13 – 600 mbar. Spectra were recorded at 295 K, 270 K, 250 K, 230 K and 210 K. The data were fitted to a polynomial expression giving the cross sections as a function of temperature and pressure.

(b) Spectra were obtained using thermostatted absorption cells with single pass optical paths of 98.1 cm and 150 cm, coupled to spectrographs having resolutions in the range 0.4–0.5 nm. Spectra were recorded at 296 K, 270 K, 250 K, 230 K and 210 K. The data were fitted to a polynomial expression giving the cross sections as a function of temperature and pressure.

(c) Spectra were obtained using a cell thermostatted at 295 K with a single path optical length of 14.0 cm and coupled to a double beam spectrophotometric system. Sample pressures in the range 0.013–1 bar were used.

(d) Quantum yields were determined by photolysis of CF_2ClBr and a reference compound in ”back-to-back” experiments. For Φ(Cl) determinations at 193 nm the reference compound was HCl and at 222 nm and 248 nm Cl atom yields were measured relative to those at 193nm. CH_3Br and C_2F_4 were used as reference compounds for measuring the yields of Br and CF_2 respectively. [Cl] and [Br] were monitored by RF and [CF_2] by long path absorption. [CF_2ClBr] and [HCl] were determined by UV absorption and [C_2F_4] by pressure measurements.

(e) Laser photolysis with photofragment translational spectroscopy using TOF-MS to detect Br, Cl and CF_2. All $CClF_2$ and $CBrF_2$ radicals produced dissociate spontaneously to produce Cl or Br + CF_2.

(f) Laser photolysis with state selected photofragment imaging. Two primary channels (2) and (3) observed with relative yields of 0.96 and 0.04. For the CF_2Cl + Br channel the branching ratio for Br($^2P_{1/2}$) and Br($^2P_{3/2}$) is determined to be 0.41±0.05.

Preferred Values

Absorption cross-sections of CF_2ClBr at 295 K and 210 K.

λ/nm	10^{20} σ/cm^2 295 K	10^{20} σ/cm^2 210 K	λ/nm	10^{20} σ/cm^2 295 K	10^{20} σ/cm^2 210 K
190	47.4	50.5	240	17.7	15.6
192	57.7	64.5	242	14.5	12.6
194	70.3	79.3	244	11.9	9.97
196	83.0	94.3	246	9.66	7.82
198	95.6	106	248	7.77	6.13
200	109	120	250	6.23	4.70
202	117	130	252	4.93	3.57
204	121	132	254	3.89	2.72
206	122	134	256	3.05	2.02
208	121	133	258	2.37	1.51
210	117	129	260	1.83	1.11
212	112	123	262	1.41	0.811
214	104	115	264	1.07	0.589
216	96.2	106	266	0.816	0.425
218	87.8	96.2	268	0.618	0.307
220	79.0	86.0	270	0.465	0.216
222	70.3	75.7	272	0.349	0.153
224	62.1	66.2	274	0.259	0.107
226	54.3	57.2	276	0.190	0.0742
228	47.3	49.0	278	0.139	0.0516
230	40.9	41.3	280	0.103	0.0355
232	35.2	34.6	282	0.075	0.0244
234	29.9	28.8	284	0.055	0.0167
236	25.4	23.7	286	0.040	0.0106
238	21.3	19.4	288	0.029	0.00721

Quantum Yields

Φ = 1.0 over the wavelength range 200–300 nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K are the mean of the values obtained in the studies of Gillotay and Simon (1989), Burkholder et al. (1991) and Orkin and Kasimovskaya (1995). Values have also been reported by Molina et al. (1982) at 5 nm intervals, and by Giolando et al. (1980) at 10 nm intervals. The agreement among these five studies (Gillotay and Simon, 1989: Burkholder et al., 1991; Orkin and Kasimovskaya, 1995; Molina et al., 1982; Giolando et al., 1980) at 295 K over the wavelength range of the preferred values is excellent. The temperature dependence of the cross-sections down to 210 K has been studied by Gillotay and Simon (1989) and by Burkholder et al. (1991) and in both cases polynomial expressions were derived giving the cross-sections as a function of temperature and wavelength. At $\lambda > 234$ nm both studies reported a decrease in absorption as the temperature was lowered. But near the absorption peak ($\sim$ 205 nm) Burkholder et al. (1991) found the cross-sections to be independent of temperature, while Gillotay and Simon (1989) found the absorption to increase with decreasing temperature, with a 20% increase at the lowest temperature studied. Furthermore, at 210 K the values of σ of Gillotay and Simon (1989) are larger than those of Burkholder et al. (1991) by $\sim$ 13% at 288 nm, increasing to $\sim$ 30% at 190 nm. Provisionally, the preferred values at 210 K are taken as the mean of the values from Gillotay and Simon (1989) and Burkholder et al. (1991).

Talukdar et al. (1996) measured the quantum yields of CF_2, Cl, and Br at 193 nm and found that the CF_2ClBr was photodissociated to give CF_2 with a quantum yield of unity, probably by initial production of CF_2Cl which was not collisionally stabilized under their conditions but went on to give CF_2 + Cl. Baum and Huber (1993), in a photofragment translational spectroscopy study, also found that at 193 nm the dominant primary process is rupture of the C-Br bond followed by decomposition of the energised CF_2Cl fragment, and a minor pathway involving initial rupture of the C-Cl bond was also detected. At 157.6 nm CF_2ClBr dissociates competitively in all three dissociation channels (2), (3 and (4), with 25% producing CF_2 directly via (4) (Yokoyama et al., 2001). At longer wavelengths photodissociation by breaking of a C-halogen bond is expected to persist with unit quantum efficiency, with direct Cl production (channel 3) decreasing to near zero at 267 nm (Huang et al., 2003).

CF_2ClBr has been estimated to have a tropospheric lifetime with respect to photolysis of 15 to 20 years (Burkholder et al., 1991; Molina et al., 1982).

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$CF_2Br_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			ΔH°/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CF_2Br_2 + h\nu$	$\rightarrow CF_2Br + Br$	(1)	280 (est)	427
	$\rightarrow CF_2 + Br + Br$	(2)	419	286
	$\rightarrow CF_2 + Br_2$	(3)	226	529

Absorption cross-section data

Wavelength range/nm	Reference	Comments
170–302	Gillotay and Simon, 1989	(a)
190–320	Burkholder et al., 1991	(b)
190–304	Orkin and Kasimovskaya, 1995	(c)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\Phi(CF_2O) = 1.14$	206.2	Molina and Molina, 1983	(d)
$\Phi(Br_2) = 1.11$			
$\Phi(-CBr_2F_2) = 1.12$			
$\Phi(CF_2) = 1.03$	247.7		
$\Phi(Br_2) = 0.99$			
$\Phi(-CBr_2F_2) = 1.05$	302.4		
$\Phi(CF_2O) = 1.23$			
$\Phi(Br_2) = 1.28$			
$\Phi(Br) = 1.96 \pm 0.25$	193	Talukdar et al., 1992	(e)
$\Phi(Br) = 1.63 \pm 0.19$	222		
$\Phi(Br) = 1.01 \pm 0.15$	248		
$\Phi(CF_2) = 1.11 \pm 0.22$	193	Talukdar et al., 1996	(e)
$\Phi(CF_2) = 1.18 \pm 0.30$	193		
$\Phi(1) = 0.84$	234	Park et al., 2001	(f)
$\Phi(2) = 0.15$			
$\Phi(3)$ = trace			
$\Phi(3) = 0.04 \pm 0.01$	248	Hsu et al., 2005	(g)

Comments

(a) Spectra were obtained using a thermostatted absorption cell with a single pass optical path of 2 m coupled to a monochromator capable of a maximum resolution of 0.015 nm. Pressures of CF_2Br_2 used covered the range 0.04–308 mbar. Spectra were recorded at 295 K, 270 K, 250 K, 230 K and 210 K. The data were fitted to a polynomial expression giving the cross sections as a function of temperature and pressure.

(b) Spectra were obtained using thermostatted absorption cells with single pass optical paths of 98.1 cm and 150 cm, coupled to spectrographs having resolutions in the range 0.4–0.5 nm. Spectra were recorded at 296 K, 270 K, 250 K, 230 K and 210 K. The data were fitted to a polynomial expression giving the cross sections as a function of temperature and pressure.

(c) Spectra were obtained using a cell thermostatted at 295 K with a single path optical length of 14.0 cm and coupled to a double beam spectrophotometric system. Sample pressures in the range 0.013–1 bar were used.

(d) Product study on photolysis of CF_2Br_2-air mixtures at 1 bar. The only photolysis products found were CF_2O and Br_2. The CF_2O and CBr_2F_2 concentrations were monitored by FTIR, and the Br_2 concentrations by UV absorption.

(e) Both of the studies of Talukdar et al. (1992; 1996) employed basically the same technique. Pulsed laser photolysis of flowing CF_2Br_2-diluent (He, N_2, or Ar) mixtures was used with a small amount of H_2 added to ensure rapid quenching of the Br($^2P_{1/2}$) produced to Br($^2P_{3/2}$). Br($^2P_{3/2}$) was detected by resonance fluorescence and CF_2 by UV absorption. The two values of $\Phi(CF_2)$ cited were obtained by monitoring [CF_2] at 248.7 and 258.3 nm. The Br($^2P_{3/2}$) measurements were calibrated by CH_3Br photolysis at the same wavelength for which a quantum yield of unity was assumed. The CF_2 measurements were calibrated using C_2F_4 photolysis taking a quantum yield for CF_2 production at 193 nm of 2.

(f) Photodissociation dynamics of CF_2Br_2 studied using 2-dimensional photofragment ion image technique, following laser photolysis at 234 and 265 nm. At 265 nm the radical channel (1) is the major primary dissociation channel.

(g) Laser photolysis at 248 nm with CRDS detection of nascent Br_2 in the $B^3\Pi+_u$- $X^1\Sigma+_g$ transition.

Preferred Values

Absorption cross-sections of CF_2Br_2 at 295 K and 210 K.

λ/nm	$10^{20}\ \sigma/cm^2$ 295 K	$10^{20}\ \sigma/cm^2$ 210 K	λ/nm	$10^{20}\ \sigma/cm^2$ 295 K	$10^{20}\ \sigma/cm^2$ 210 K
190	117	130	250	58.3	55.3
192	110	122	252	46.5	39.1
194	102	110	254	36.8	29.9
196	91.4	97.8	256	28.9	22.6
198	82.1	86.3	258	22.4	17.0
200	74.8	78.4	260	17.3	12.5
202	71.7	74.5	262	13.1	9.17
204	73.4	77.1	264	9.90	6.66
206	80.9	85.2	266	7.47	4.81
208	92.3	100	268	5.59	3.44
210	110	120	270	4.17	2.44
212	134	145	272	3.08	1.72
214	155	173	274	2.27	1.21
216	180	202	276	1.66	0.844
218	205	230	278	1.21	0.588
220	226	254	280	0.888	0.406
222	244	273	282	0.647	0.281
224	253	282	284	0.470	0.194
226	257	283	286	0.336	0.129
228	253	277	288	0.245	0.0891
230	245	264	290	0.177	0.0616

λ/nm	10^{20} σ/cm^2 295 K	10^{20} σ/cm^2 210 K	λ/nm	10^{20} σ/cm^2 295 K	10^{20} σ/cm^2 210 K
232	230	245	292	0.128	0.405
234	212	222	294	0.093	0.277
236	192	197	296	0.067	0.185
238	170	171	298	0.049	0.127
240	147	145	300	0.035	0.0083
242	126	121	302	0.025	0.0056
244	106	99.3	304	0.018	0.0011
246	87.8	86.4	306	0.013	
248	72.0	64.1	308	0.009	

Quantum Yields

$\Phi = (\Phi_1 + \Phi_2 + \Phi_3) = 1.0$ over the range 200–310 nm.

Comments on Preferred Values

The preferred values for the absorption cross-sections at 295 K are the means of the values reported by Gillotay and Simon (1989), Burkholder et al. (1991) and Orkin and Kasimovskaya (1995). Values at 5 nm intervals have also been reported by Molina et al. (1982). The agreement among the four studies (Gillotay and Simon, 1989; Burkholder et al., 1991; Orkin and Kasimovskaya, 1995; Molina et al.,1982) over the wavelength range of the preferred values is very good although discrepancies appear at longer wavelengths. The temperature dependence down to 210 K has been studied by Gillotay and Simon (1989) and Burkholder et al. (1991). There is only fair agreement between the two studies. At $\lambda > 250$ nm both report a decrease in absorption as the temperature is lowered (Gillotay and Simon, 1989; Burkholder et al., 1991), and near the absorption peak (about 230 nm) both studies find an 11% increase in absorption in going to the lowest temperature. However, although the values of σ from the two studies are in good agreement close to the absorption maximum they steadily diverge on moving to longer and shorter wavelengths reaching a 30% difference at 190 nm and a factor of 2 at 300 nm. Provisionally, the preferred values at 210 K are taken as the mean of the values from Gillotay and Simon (1989) and Burkholder et al. (1991).

Molina and Molina (1983) found that the only products of photolysis of CF_2Br_2-air mixtures at a pressure of 1 bar were CF_2O and Br_2 and concluded that the quantum yield for photodissociation of CBr_2F_2 was unity over the wavelength range 200–300 nm. This is supported by the findings of Talukdar et al. (1992; 1996). The preferred values for the quantum yields are based on the studies of Molina and Molina (1983) and Talukdar et al. (1992; 1996). Molecular beam (Krajnovich et al., 1984) and spectroscopic studies (Gosnell et al., 1991; Vatsa et al., 1995) at 248 nm have detected the transient CF_2Br. Cameron et al. (2000) used LIF to detect vibrational distribution of nascent CF_2 produced by photolysis of CBr_2F_2 at discrete wavelegths in the range 223–260 nm. Their results showed that CF_2 production at 246 nm was accompanied by the production of two Br fragments. However Hsu et al (2005) measured significant Br_2 production ($\phi = 0.04$) at 248 nm using CRDS detection, and Park et al (2001) report seeing a Br_2 elimination channel at 234 nm. Here is insufficient information to recommend λ dependence of ϕ(Br), but it is recommended to use $\phi(\mathrm{Br}) = 1.0$ for tropospheric photolysis and $\phi(\mathrm{Br}) = 2.0$ for stratospheric photolysis.

Because its absorption extends into the 290–310 nm wavelength range, CF_2Br_2 has a short tropospheric lifetime with respect to photolysis, of about 3 years.

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$CHBr_3$ + h$\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CHBr_3$ + hν	$\rightarrow CHBr_2 + Br$	(1)	276	433
	$\rightarrow CHBr + Br_2$	(2)	355	337

Absorption cross-section data

Wavelength range/nm	Reference	Comments
170–310	Gillotay and Simon, 1989	(a)
286–362	Moortgat et al., 1993	(b)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\Phi(Br) = 0.74$	234	Xu et al., 2002	(c)
$\Phi(Br_2) = 0.26$			
$\Phi(Br) = 0.84$	267		
$\Phi(Br_2) = 0.16$			
$\Phi(Br) = 1.0$	302-306	Bayes et al., 2003	(d)
$\Phi(Br) = 0.76 \pm 0.03$	266		
$\Phi(Br_2) = 0.23 \pm 0.05$	248	Huang et al., 2004	(e)

Comments

(a) Two different techniques were used. One employed a cell with a fixed optical path of 2 m and an evacuated monochromator capable of reaching wavelengths down to 170 nm. In the other a multiple reflection cell with optical paths up to 5 m was used. In both cases the cells were thermostatted and measurements were made in the range 295–240 K.

(b) Measurements were made using two pieces of apparatus. In one a cell of 63 cm fixed path length was used and measurements made at 296 K. The other contained multiple pass optics with a total path length of 980 cm. The latter system was used for measurements at 296 K, 286 K, 266 K, and 256 K.

(c) Photodissociation dynamics of $CHBr_3$ studied using photofragment TOF-MS and velocity ion image imaging, following laser photolysis at 234 and 265 nm. Both excited spin orbit excited $Br(^2P_{1/2})$ and ground $Br(^2P_{3/2})$ were found by REMPI, and VUV photoionisation at 118 nm to detect radical products.

(d) Photolysis of using PLP with joule meter to measure the average pulse energy. Br detected by VUV-RF at discrete λ between 130–163 nm.

(e) Laser photolysis at 248 nm with CRDS detection of nascent Br_2 in the $B^3\Pi+_u$ - $X^1\Sigma+_g$ transition.

Preferred Values

Absorption cross-sections of $CHBr_3$ at 296 K and 210 K.

λ/nm	10^{20} σ/cm^2 295 K	10^{20} σ/cm^2 210 K	λ/nm	10^{20} σ/cm^2 295 K	10^{20} σ/cm^2 210 K
190	399	393	270	30.8	21.1
192	360	351	272	24.8	16.5
194	351	353	274	19.8	12.8
196	366	383	276	15.8	9.94
198	393	422	278	12.5	7.66
200	416	466	280	9.88	5.88
202	433	475	282	7.77	4.50
204	440	474	284	6.10	3.42
206	445	467	286	4.81	2.60
208	451	471	288	3.75	1.97
210	468	490	290	2.88	1.49
212	493	522	292	2.22	1.05
214	524	551	294	1.70	0.757
216	553	593	296	1.28	0.547
218	574	621	298	0.951	0.395
220	582	633	300	0.719	0.285
222	578	623	302	0.530	0.206
224	558	597	304	0.394	0.149
226	527	562	306	0.298	0.107
228	487	516	308	0.226	0.078
230	441	465	310	0.171	0.060
232	397	409	312	0.127	0.040
234	362	362	314	0.095	0.029
236	324	324	316	0.071	0.021
238	295	295	318	0.053	0.015
240	273	272	320	0.039	0.011
242	253	250	322	0.029	0.0079
244	234	224	324	0.021	0.0057
246	214	202	326	0.016	0.0041
248	194	178	328	0.009	0.0030
250	174	157	330	0.009	0.0022
252	158	138	332	0.007	0.0016
254	136	116	334	0.005	0.0011
256	116	96.2	336	0.004	0.00081
258	98.6	79.5	338	0.003	0.00059
260	82.8	64.7	340	0.002	0.00042
262	68.9	52.5			
264	56.9	42.2			
266	46.7	33.7			
268	38.0	26.7			

Comments on Preferred Values

There have been two studies of the absorption cross-sections of $CHBr_3$. Gillotay et al. (1989) reported values over the wavelength range 170–310 nm and the temperature range 295–240 K; Moortgat et al. (1993) reported values over the range 245–360 nm and the temperature range 296–256 K. In the region where the measurements overlap, the agreement is very good. The preferred values at 296 K are those reported by Gillotay et al. (1989) over the wavelength range 190–284 nm and those reported by Moortgat et al. (1993) at longer wavelengths. The preferred values at 210 K are those of Gillotay et al. (1989) over the range 190–298 K, which they obtained by extrapolation of their higher temperature results, and those over the range 290–340 K are from the expression, $\ln \sigma(\lambda,T)$ = (0.0618350 - 0.000241014 λ)(273-T) - (2.37616 + 0.1475688 λ), which was derived by Moortgat et al. (1993) from a fit to the combined data of their study and that of Gillotay et al. (1989). It is valid in the wavelength range 290–340 nm and the temperature range 300–210 K.

The quantum yield for the formation of Br atoms determined by Bayes et al. (2003) for 303 to 306 nm, the Br-atom quantum yield was unity within experimental error. At longer wavelengths, the quantum yields decreases to 0.76 at 324 nm, but the authors claim that the lower than unity values are the result of systematic and random errors and/or incorrect absorption cross sections. Support for unity quantum yield at $\lambda >$300 nm comes from theoretical calculations by Peterson and Francisco (2002), and is recommended for modeling in the troposphere.

Bayes et al. (2003) also report a Br-atom quantum yield of 0.76 ± 0.03 at 266 nm, indicating that another photodissociation channel becomes important. This confirms the result of Xu et al. (2002) who measured atomic Br and molecular Br_2 by TOF mass spectrometry from bromoform photolysis at 234 and 267 nm. Huang (2004) also observed Br_2 production at 248 nm, using CRDS to probe the molecular fragment, and measured a quantum yield of 0.23±0.05. On the other hand the experiments of McGivern et al. (2000) and Zou et al. (2004), using VUV ionisation photofragment translational spectroscopy at 193 nm and at 248 nm respectively, suggest that Br_2 fragments do not arise from a single photon channel, and that channel (1) is the only primary process. In view of these inconsistencies we are unable to recommend Br atom quantum yields for $\lambda <$300 nm. Note that regardless of whether Br or Br_2 are formed, any Br_2 will be rapidly photodissociated to 2Br in the sunlit atmosphere.

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IV.A4.264

CF_2BrCF_2Br + hν → products

Primary photochemical processes

Reaction		ΔH°/kJ mol^{-1}	$\lambda_{threshold}$/nm
CF_2BrCF_2Br + hν	→ CF_2BrCF_2 + Br	280 (est)	427

Absorption cross-section data

Wavelength range/nm	Reference	Comments
170–302	Gillotay et al., 1988	(a)
190–320	Burkholder et al., 1991	(b)
190-304	Orkin and Kasimovskaya, 1995	(c)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
Φ(Br) = 1.9 ± 0.1	193	Zou et al., 2000	(d)
Φ(Br) = 1.9 ± 0.1	233		
Φ(Br) = 1.4 ± 0.1	266		

Comments

(a) Spectra were obtained using a thermostatted absorption cell with a single pass optical path of 2 m coupled to a monochromator capable of a maximum resolution of 0.015 nm. Spectra were recorded at 295 K, 270 K, 250 K, 230 K and 210 K. The data were fitted to a polynomial expression giving the cross sections as a function of temperature and pressure.

(b) Spectra were obtained using a thermostatted absorption cells with single pass optical paths of 98.1 cm and 150 cm, coupled to spectrographs having resolutions in the range 0.4–0.5 nm. Spectra were recorded at 296 K, 270 K, 250 K, 230 K and 210 K. The data were fitted to a polynomial expression giving the cross sections as a function of temperature and pressure.

(c) Spectra were obtained using a cell thermostatted at 295 K with a single path optical length of 14.0 cm and coupled to a double beam spectrophotometric system. Sample pressures in the range 0.65–160 mbar were used.

(d) Product branching ratios, angular and translational distributions measured using photofragment translational spectroscopy, following laser photodissociation of CF_2BrCF_2Br. Detection by VUV ionisation or REMPI.

Preferred Values

Absorption cross-sections of CF_2BrCF_2Br at 296 K and 210 K.

λ/nm	10^{20} σ/cm^2 295 K	10^{20} σ/cm^2 210 K
190	108	119
192	114	124
194	119	128
196	123	131
198	125	133
200	125	133
202	125	132
204	121	129
206	117	125
208	112	119
210	105	112
212	98.6	104
214	94.5	96.1
216	83.4	85.0
218	75.6	79.0
220	67.8	70.3
222	60.2	62.0
224	53.0	54.3
226	46.2	46.8
228	40.0	40.1
230	34.2	33.9
232	29.0	27.9
234	24.3	22.6
236	20.1	18.2
238	16.5	14.5
240	13.4	11.5
242	10.7	8.95
244	8.47	6.89
246	6.69	5.25
248	5.23	2.95
250	4.05	2.93
252	3.09	2.15
254	2.36	1.56
256	1.77	1.13
258	1.32	0.807
260	0.978	0.576
262	0.724	0.391
264	0.535	0.275
266	0.394	0.191
268	0.290	0.134
270	0.212	0.093
272	0.155	
274	0.112	
276	0.082	
278	0.060	
280	0.044	

Quantum Yields

Φ (Br) = 2 (in stratosphere).
Φ (Br) = 1 (in troposphere).

Comments on Preferred Values

The preferred values for the absorption cross-sections at 295 K are the means of the values reported by Gillotay et al. (1988), Burkholder et al. (1991) and Orkin and Kasimovskaya (1995). Values at 5 nm intervals have also been reported by Molina et al. (1982). The agreement among the four studies (Gillotay et al., 1988; Burkholder et al., 1991; Orkin and Kasimovskaya, 1995; Molina et al., 1982) over the wavelength range of the preferred values is very good. The temperature dependence down to 210 K has been studied by Gillotay et al. (1988) and Burkholder et al. (1991). There are significant differences between the two studies (Gillotay et al.,1988; Burkholder et al., 1991). Close to the absorption peak (∼200 nm) Burkholder et al. (1991) report a 20% increase in the absorption cross-section in going from 295 K to 210 K, whereas Gillotay et al. (1988) report a small decrease. Furthermore, at 210 K the values of the cross-section obtained by Gillotay et al. (1988) are only ∼4% lower than those of Burkholder et al. (1991) at short wavelengths but this difference increases in going to longer wavelengths, reaching ∼40% at 270 nm. Provisionally, the preferred values at 210 K are taken as the mean of the values of Gillotay et al. (1988) and Burkholder et al. (1991).

Photolysis is expected to occur with unit quantum efficiency by rupture of the C-Br bond to give CF_2BrCF_2 + Br and prompt dissociation of nascent CF_2BrCF_2 to give a second Br atom is likely to predominate in stratospheric photolysis, which is the main atmospheric sink. CF_2BrCF_2Br has been estimated to have a tropospheric lifetime against direct solar photolysis of 34 years (Burkholder et al., 1991).

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IV.A4.265

$CH_2Br_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		ΔH°/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CH_2Br_2 + h\nu$	$\rightarrow CH_2Br + Br$	292	410

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–300	Molina et al., 1982	(a)
174–290	Gillotay et al., 1988	(b)
215-300	Mössinger et al., 1998	(c)

Quantum yield data

No experimental data are available.

Comments

(a) The cross-sections were measured using a double beam spectrophotometer equipped with 10 cm and 180 cm cells. Pressures in the range 8–52 mbar were used.

(b) Spectra were obtained using a thermostatted absorption cell with a single pass optical path of 2 m coupled to a monochromator capable of a maximum resolution of 0.015 nm. Pressures of CH_2Br_2 used covered the range 0.05–47 × 10^{-2} mbar. Spectra were recorded at 295 K, 270 K, 250 K, 230 K and 210 K.

(c) Spectra were obtained using a thermostatted absorption cell of optical path length 100 cm coupled to a double beam optical system giving a resolution of ∼ 0.6 nm. Pressures used were in the range 0.13–53 mbar. Absorption measurements were made at 348 K, 328 K, 298 K, 273 K and 250 K. At each wavelength the temperature dependence of the cross-sections was expressed as $\ln \sigma_T = \ln \sigma_{298\,K} + B(T - 298)$ and values of B were derived.

Preferred Values

Absorption cross-sections of CH_2Br_2 at 298 K and 210 K.

λ/nm	$10^{20}\ \sigma/cm^2$ 298 K	$10^{20}\ \sigma/cm^2$ 210 K	λ/nm	$10^{20}\ \sigma/cm^2$ 298 K	$10^{20}\ \sigma/cm^2$ 210 K
200	226	223	255	14.1	8.51
205	215	206	260	6.61	3.38
210	235	240	265	3.03	1.34
215	263	325	270	1.34	0.506
220	272	356	275	0.514	0.199
225	247	318	280	0.255	0.0773
230	196	239	285	0.114	0.0324
235	139	154	290	0.0499	0.0140
240	88.6	86.1	295	0.0165	0.0049
245	51.9	43.6	300	0.006	0.0013
250	28.0	19.7			

Quantum Yields

Φ (Br) = 1 for $\lambda > 240$ nm.

Comments on Preferred Values

The preferred values for the absorption cross-sections at 298 K are the means of the values reported by Molina et al. (1982), Gillotay et al. (1988) and Mössinger et al. (1998). The agreement among the three studies (Molina et al., 1982; Gillotay et al., 1988; Mössinger et al., 1998) over the wavelength range of the preferred values is excellent. The temperature dependence of σ over the range 210–295 K has been studied by Gillotay et al. (1988) and over the range 250–348 K by Mössinger et al. (1998). The results agree well in the region where they overlap and both find that σ increases with decreasing temperature at the absorption band maximum (219 nm) but shows a decrease with temperature decrease in the long wavelength tail of the spectrum. The preferred values at 210 K are those of Gillotay et al. (1988) which are in very good agreement with the values calculated from the expression and temperature coefficients of Mössinger et al. (1998), based on their measurements in the range 250–348 K.

There are no quantum yield measurements but an investigation of the photodissociation at 248 nm using product translational spectroscopy shows that CH_2Br_2 undergoes a simple C-Br fission (Lee et al., 2003).

References

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Appendix 4: IO_x Reactions

IV.A4.266

$$\mathbf{HO + CH_3I \rightarrow H_2O + CH_2I}$$

ΔH° = -63.1 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$3.1 \times 10^{-12} \exp[-(1119 \pm 205)/T]$	271-423	Brown et al., 1990	DF-RF
$(7.2 \pm 0.7) \times 10^{-14}$	298		
$(1.2 \pm 0.4) \times 10^{-13}$	299	Gilles et al., 1996	PLP-LIF (a)
$(9.9 \pm 2.0) \times 10^{-14}$	298 ± 2	Cotter et al., 2003	DF-RF

Comments

(a) Derived from the time-concentration profiles of HO radicals monitored by LIF after generation of $O(^3P)$ atoms (from 193 nm pulsed laser photolysis of N_2O in N_2) in the presence of varying amounts of CH_3I.

Preferred Values

$k = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.3 \times 10^{-12} \exp(-1120/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270-430 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The room temperature rate coefficients of Brown et al. (1990), Gilles et al. (1996) and Cotter et al. (2003) are in reasonable agreement, and the preferred 298 K rate coefficient is an average of the room temperature rate coefficients from these three studies. The temperature dependence obtained by Brown et al. (1990), the only temperature-dependent study to date, is accepted and the pre-exponential factor is adjusted to fit the 298 K preferred value.

References

Brown, A. C., Canosa-Mas, C. E. and Wayne, R. P.: Atmos. Environ., 24A, 361, 1990.
Cotter, E. S. N., Canosa-Mas, C. E., Manners, C. R., Wayne, R. P. and Shallcross, D. E.: Atmos. Environ., 37, 1125, 2003.
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IV.A4.267

HO + CF_3I → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.2) \times 10^{-13}$	295	Garraway and Donovan, 1979	FP-RA
$(3.1 \pm 0.5) \times 10^{-14}$	300	Brown et al., 1990	DF-RF
$5.8 \times 10^{-12} \exp[-(1359 \pm 133)/T]$	281-443	Berry et al., 1998	FP-RF (a)
$(5.9 \pm 1.4) \times 10^{-14}$	292		
$2.1 \times 10^{-11} \exp[-(2000 \pm 140)/T]$	271-370	Gilles et al., 2000	PLP-LIF (b)
$(2.35 \pm 0.54) \times 10^{-14}$	296		

Comments

(a) The measured rate coefficients were observed to increase with flash energy (which affects both the initial concentration of HO radicals and the amount of CF_3I photolysis products). The cited rate coefficients at each temperature were obtained from extrapolation to zero flash energy. Theoretical calculations indicated that the dominant channel is that to form CF_3 + HOI.

(b) No effect on the rate coefficient of varying the laser fluence by a factor of ∼5 was observed when 351 nm pulsed laser photolysis of HONO was used as the HO radical source. However, a significant effect of laser fluence was observed when using 248 nm pulsed laser photolysis of O_3 in the presence of H_2O to generate HO radicals. The cited rate coefficients and Arrhenius expression were obtained from experiments using 351 nm photolysis of HONO as the HO radical source. The CF_3I concentrations were monitored by UV/visible absorption spectroscopy.

Preferred Values

$k = 2.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.1 \times 10^{-11} \exp(-2000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270-370 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

Studies of this reaction have the potential for secondary reactions (including, in the pulsed photolysis systems, with CF_3I photolysis products), reactions with impurities, and/or heterogeneous wall reactions (Brown et al., 1990; Wayne et al., 1992; Berry et al., 1998; Gilles et al., 2000). The preferred values are based on the more extensive study of Gilles et al. (2000) in which HONO photolysis at 351 nm was used to generate HO radicals with no apparent problems due to secondary reactions and with the CF_3I concentrations being monitored by UV/visible absorption spectroscopy.

References

Berry, R. J., Yuan, J., Misra, A. and Marshall, P.: J. Phys. Chem. A, 102, 5182, 1998.
Brown, A. C., Canosa-Mas, C. E. and Wayne, R. P.: Atmos. Environ., 24A, 361, 1990.
Garraway, J. and Donovan, R. J.: J. Chem. Soc., Chem. Comm. 1108, 1979.
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Wayne, R. P., Canosa-Mas, C. E., Heard, A. C. and Parr, A. D.: Atmos. Environ., 26A, 2371, 1992.

IV.A4.268

$$\mathbf{CH_2IO_2 + CH_2IO_2 \rightarrow CH_2IOH + HC(O)I + O_2 \quad (1)}$$
$$\mathbf{\rightarrow 2CH_2IO + O_2 \quad (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\sim 9 \times 10^{-11}$	295 ± 2	Sehested et al., 1994	(a)

Comments

(a) Pulse radiolysis UV absorption spectrometric study of CH_3I-O_2-SF_6 mixtures at a total pressure of 1000 mbar. CH_2IO_2 radicals were monitored by UV absorption with $\sigma_{370} = (2.1 \pm 0.5) \times 10^{-18}$ cm^2 molecule^{-1}. The interpretation of the kinetic data is complicated by the presence of CH_3O_2 radicals, which leads to mixed-order kinetics. The above approximate value of k was derived on the basis of several assumptions.

Preferred Values

No recommendation

Comments on Preferred Values

The approximate and exceptionally large rate coefficient obtained by Sehested et al. (1994) should be regarded with caution owing to the inherent complications in their experimental system. Until more work is carried out in this reaction, we make no recommendation.

References

Sehested, J., Ellermann, T. and Nielsen, O. J.: Int. J. Chem. Kinet. 26, 259, 1994.

IV.A4.269

$CH_3I + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			ΔH°/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CH_3I + h\nu$	$\rightarrow CH_3 + I(^2P_{3/2})$	(1)	239	541
	$\rightarrow CH_3 + I(^2P_{1/2})$	(2)	330	362
	$\rightarrow CH_2 + HI$	(3)	403	297

Absorption cross-section data

Wavelength range/nm	References	Comments
210–360	Jenkin et al., 1993	(a)
160–400	Fahr et al., 1995	(b)
200-380	Roehl et al., 1997	(c)
235-350	Rattigan et al., 1997	(d)

Quantum yield data

Measurement	Wavelength range/nm	References	Comments
$\Phi(I_2)$	254	Christie, 1958	(e)
$\Phi\{I(^2P_{1/2}); I(^2P_{3/2})\}$	266	Riley and Wilson, 1972	(f)
$\Phi\{I(^2P_{1/2})\}$	248-308	Baughcum and Leone, 1980	(g)
$\Phi\{I(^2P_{1/2}); I(^2P_{3/2})\}$	247.5-312.5	Hunter et al., 1983	(h)
$\Phi I(^2P_{1/2})=0.07 \pm 0.02$	304	Li et al., 2005	(i)
$\Phi I(^2P_{3/2})=0.93 \pm 0.02$	304		

Comments

(a) The absorption spectrum of CH_3I was recorded by diode array spectroscopy with a resolution of approx. 1 nm using a purified sample. Tabulated cross section values for the indicated range were given, showing a single absorption band extending from 210 to 365 nm. The absolute cross-section at the maximum of absorption at 257.9 nm was $\sigma = 1.22 \times 10^{-18}$ cm^2 molecule^{-1}, which was in good agreement with the earlier published spectrum of Porret and Goodeve (1937).

(b) Absorption spectrum measured over temperature range 223–333 K at a resolution of 0.1 nm; cross sections at 0.5 nm intervals given. In addition to the gas phase measurements over the wavelength range 160–335 nm, liquid phase measurements over the range 330–400 nm were also reported. A wavelength shift was applied to convert the liquid phase data to accurate gas phase cross sections at the long wavelengths.

(c) Absorption coefficients for CH_3I were determined by diode array spectrometry with a spectral resolution of 0.6 nm. Tabulated cross section values for the indicated range were given. A single absorption band was observed to extend from $<$ 230 nm to 365 nm with a maximum at 260 nm where the absorption cross section was $\sigma = (1.09\pm0.08) \times 10^{-18}$ cm^2 molecule^{-1} at 298 K. The temperature dependence of the absorption cross section was determined over the range 243–333 K; broadening of the band was observed giving a significant decline in σ with decreasing temperature in the tropospheric photolysis region ($\lambda > 290$ nm).

(d) The absorption spectrum of CH_3I (purity $>$ 98%) was recorded by diode array spectrometry with a resolution of 0.3 nm. Tabulated cross section values for the indicated range were given. The absolute cross-section at the maximum of absorption at 260 nm was $\sigma = 1.13 \times 10^{-18}$ cm^2 molecule^{-1} with a stated overall uncertainty of ±5%. Significant temperature dependence of the absorption cross section was observed over the range 228–298 K, with a decrease in σ with decreasing temperature in the long wavelength tail. A second absorption band is indicated by an increase in σ below 210 nm.

(e) Photo-oxidation of CH_3I; measurement of loss of CH_3I and yield of I_2 product.
$\Phi(\text{-}CH_3I) = 1.0$; $\Phi(I_2) = 0.5$.

(f) Translational energy of the I atoms produced in 266 nm photolysis of CH_3I in a molecular beam. Suggested the following primary processes:
$CH_3I + h\nu \rightarrow CH_3 + I(^2P_{3/2})$
$CH_3I + h\nu \rightarrow CH_3 + I(^2P_{1/2})$
with $I(^2P_{3/2})$ production at 78% of the primary process.

(g) Pulsed tunable laser photolysis of CH_3I, with $I(^2P_{1/2})$ detection by infra-red fluorescence at 1.315 μm. $\Phi\{I(^2P_{1/2})\}$ increased from 0.05 to 0.81 over the wavelength range 308–248 nm.

(h) Branching ratio for $I(^2P_{1/2})/I(^2P_{3/2})$ as a function of wavelength determined by an optical acoustic method.

(i) Crossed beam Laser photolysis - core sampling photofragment translational spectroscopy study. $I(^2P_{1/2})$ and $I(^2P_{3/2})$ detected by REMPI + pulsed acceleration TOF MS, giving high kinetic resolution. The $\Phi I(^2P_{1/2})$ 2 + 1 is determined relative to the total I atom yield, using a calibration method reported by Kang et al. (1996).

Preferred Values

Absorption cross-sections of CH_3I at 298 K

Wavelength/nm	$10^{20}\ \sigma/\text{cm}^2$	$10^3\ B/\text{K}^{-1}$
205	7.0	
210	3.8	
215	5.2	
220	6.9	
225	9.1	
230	12.6	
235	20.2	0.67
240	37.4	0.61
245	63.6	0.34
250	92.1	0.08
255	111.1	-0.1
260	112.3	-0.12
265	96.6	0.1
270	71.7	0.54
275	47.1	1.33
280	28.0	2.43
285	15.2	3.74
290	7.79	4.98
295	3.92	6.38
300	2.03	6.97
305	1.09	6.82
310	0.619	6.78
315	0.356	6.95

Wavelength/nm	10^{20} σ/cm^2	10^3 B/K^{-1}
320	0.215	6.94
325	0.124	6.79
330	0.070	7.82
335	0.033	9.34
340	0.023	10.95
345	0.0127	13.58
350	0.0067	16.83
355	0.0026	18.91
360	0.0013	17.28
365	0.0004	23.63

Temperature dependence given by: $\ln \sigma = \ln \sigma(298) + B(T\text{-}298/\mathrm{K})$

Quantum Yield

$\Phi_1 + \Phi_2 = 1.0$ over the wavelength range 210–360 nm.

Comments on Preferred Values

Porret and Goodeve (1937) measured the absolute absorption cross-sections of methyl iodide in the range 200–360 nm in their pioneering work on the quantitative investigation of electronic spectra of simple molecules. The first absorption band extends from 360 nm to ~ 210 nm and is attributed to a $\sigma \rightarrow$ n transition. The reported cross sections of Jenkin et al. (1993), Rattigan et al. (1997) and Roehl et al. (1997) are in good agreement with each other and with those in the earlier published study (Porret and Goodeve, 1937). The results of Fahr et al. (1995) agree well with the other measurements at $\lambda > 300$ nm, but are significantly higher by ~20% at the maximum of absorption. The preferred values for the cross-sections at 298 K are based on the data for the absolute absorption cross-sections reported by Jenkin et al. (1993), Rattigan et al. (1997) and Roehl et al. (1997). The listed values are actual values at 1 nm intervals.

The effect of temperature on the absorption cross-section has been studied by Fahr et al. (1995), Rattigan et al. (1997) and Roehl et al. (1997). All studies show excellent agreement for the temperature dependence and reveal an apparent narrowing of the band as temperature decreases, leading to an increase in σ at the band head and a decrease in σ in the long wavelength tail of absorption. The temperature dependence of CH_3I absorption has also been investigated by Waschewsky et al. (1996) who argue that the temperature-dependent cross section measurements are complicated by the presence of dimers and therefore do not apply to atmospheric spectra. Analysis by Rattigan et al. (1997) and Roehl et al. (1997) of their measurements taken over an extensive range of pressures and temperatures shows that the effect of dimers must be completely negligible for their experimental conditions. The recommended temperature dependence, expressed in terms of a single parameter B in the equation: $\ln \sigma = \ln \sigma(298) + B(T\text{-}298/\mathrm{K})$ from the work of Rattigan et al. (1997) is adopted.

The photochemistry of alkyl iodides has been extensively studied since the early investigations of photolytic reactions and has been reviewed by Majer and Simons (1964), Calvert and Pitts (1966) and Okabe (1978). For methyl iodide the primary process is dissociation into a methyl radical and an iodine atom, processes (1) and (2), occurring with a quantum yield of unity. Reaction (3) may be important following absorption in the vacuum uv (Riley and Wilson, 1972).

The primary photodissociation processes have been studied extensively in conjunction with the laser emission: $I(^2P_{1/2}) \rightarrow I(^2P_{3/2}) + h\nu$ observed at 1.315 μm in the near-UV flash photolysis of CH_3I (Kasper and Pimentel, 1964). State-selected photofragment spectroscopy has shown that I atoms are produced in both the ground $I(^2P_{3/2})$ and the electronically excited $I(^2P_{1/2})$ state. The relative yields of $I(^2P_{1/2})$ increases with decreasing wavelength below 304 nm to a maximum near the maximum in the A-band absorption of CH_3I near 260 nm. This can be rationalised in terms of the correlations of $I(^2P_{1/2})$ and $I(^2P_{3/2})$ states with the $^3Q_{o+}$, $^1Q_1$ and $^3Q_1$ electronic states, which have λ_{max} at 261 nm, 240 nm and 300 nm respectively (Gedanken et al., 1975).

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IV.A4.270

$CF_3I + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			ΔH°/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CF_3I + h\nu$	$\rightarrow CF_3 + I(^2P_{3/2})$	(1)	230	521
	$\rightarrow CF_3 + I(^2P_{1/2})$	(2)	320	374

Absorption cross-section data

Wavelength range/nm	References	Comments
216–370	Solomon et al., 1994	(a)
160–340	Fahr et al., 1995	(b)
235–400	Rattigan et al., 1997	(c)

Quantum yield data

Measurement	Wavelength range/nm	References	Comments
$\Phi\{I(^2P_{1/2}); I(^2P_{3/2})\}$	266	Riley and Wilson, 1972	(d)
$\Phi\{I(^2P_{1/2}); I(^2P_{3/2})\}$	304	Kang et al., 1996	(e)
$\Phi\{I(^2P_{1/2}); I(^2P_{3/2})\}$	275-303	Furlan et al., 1996	(f)

Comments

(a) Absorption coefficients for purified CF_3I determined by diode array spectrometry, over temperature range 200–298 K. A single absorption band was observed to extend from 370–210 nm with a maximum at 267 nm where the absorption coefficient was $\sigma = 6.0 \times 10^{-18}$ cm^2 $molecule^{-1}$.

(b) The absorption spectrum of CF_3I was recorded by diode array spectrometry with a resolution of approx. 1 nm using a purified sample. The absolute cross-section at the maximum of absorption at 267 nm was $\sigma = 6.8 \times 10^{-18}$ cm^2 $molecule^{-1}$. A second band extends into the vacuum UV. The temperature dependence over the wavelength range 160–240 nm was determined at 240, 295 and 355 K; and over the range 240–350 nm for 218–333 K.

(c) The absorption spectrum of CF_3I was recorded by diode array spectrometry with a resolution of approx. 0.6 nm using a purified sample. The absolute cross-section at the maximum of absorption at 267 nm was $\sigma = (6.0 \pm 0.1) \times 10^{-18}$ cm^2 $molecule^{-1}$. A second band extends into the vacuum UV. The temperature dependence was determined for 243–333K.

(d) Translational energy of the I atoms produced in 266 nm photolysis of CF_3I in a molecular beam. Suggested the following primary processes:
$CF_3I + h\nu \rightarrow CF_3 + I(^2P_{3/2})$
$CF_3I + h\nu \rightarrow CF_3 + I(^2P_{1/2})$
with $I(^2P_{3/2})$ production at 78% of the primary process.

(e) Relative yield of $I(^2P_{1/2})/I(^2P_{3/2})$ determined by (2+1) REMPI and pulsed field TOF-MS following laser photodissociation of CF_3I. $\Phi\{I(^2P_{1/2})\} = 0.69$.

(f) Relative yield of $I(^2P_{1/2})/I(^2P_{3/2})$ obtained by high resolution photofragment translational spectrometry using pulsed laser photolysis and TOF-MS. $\Phi\{I(^2P_{1/2})\}$ increased from 0.38 at 303 nm to 0.92 at 275 nm.

Preferred Values

Absorption cross-sections of CF_3I at 298 K

Wavelength/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	$10^3\ B/\mathrm{K}^{-1}$
235	7.5	0.155
240	13.4	0.21
245	21.4	-0.121
250	32.5	-0.45
255	45.5	-0.766
260	57.3	-0.992
265	64.2	-1.07
270	63.9	-0.936
275	56.9	-0.554
280	45.6	-0.0505
285	33.8	1.02
290	23.0	2.18
295	14.6	3.34
300	8.81	4.56
305	5.13	5.81
310	2.88	6.82
315	0.907	7.89
325	0.49	8.22
330	0.263	8.57
335	0.144	9.06
340	0.0771	9.98
345	0.0393	10.9
350	0.0208	12.5
355	0.0115	13.3
360	0.0064	14.6
365	0.0036	14.6
370	0.002	15.5
375	0.0011	17.1
380	0.0007	17.7
385	0.0004	19.7
390	0.0001	22.6

Temperature dependence given by: $\ln \sigma = \ln \sigma(298) + B(T\text{-}298/\mathrm{K})$

Quantum Yield

$\Phi_1 + \Phi_2 = 1.0$ over the wavelength range 210–360 nm.

Comments on Preferred Values

There is excellent agreement between all three reported data sets for the cross section and its temperature dependence. The maximum of the first absorption band is lower and red-shifted compared with methyl iodide. The band narrowed with decreasing temperature leading to a significant decrease in the cross section in the long wavelength tail; at 320 nm the value decreases by nearly 50% at 200 K. The recommended values for σ and its temperature dependence are the mean of all three studies (Solomon et al., 1994; Fahr et al., 1995; Rattigan et al. 1997).

Photolysis is expected to occur with quantum efficiency by breaking of the C-I bond to yield CF_3 + I. State-selected photofragment spectroscopy has shown that I atoms are produced predominantly in the excited state $I(^2P_{1/2})$, following photodissociation of CF_3I near the band maximum. The branching ratio for: $I(^2P_{1/2})/I(^2P_{3/2})$ production decreases at longer wavelengths but there is some disagreement in the actual values (Riley and Wilson, 1972; Kang et al., 1996; Furlan et al., 1996).

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IV.A4.271

$CH_2ClI + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°/kJ\ mol^{-1}$	$\lambda_{threshold}$/nm
$CH_2ClI + h\nu$	$\rightarrow CH_2Cl + I$	(1)	217	551
	$\rightarrow CH_2I + Cl$	(2)	344	347

Absorption cross-section data

Wavelength range/nm	Reference	Comments
235–390	Rattigan et al., 1997	(a)
200–380	Roehl et al., 1997	(b)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\Phi(I_2)$	266	Schmitt and Comes, 1987	(c)
$\Phi\{I(^2P_{1/2})\} = 0.44$	222	Senapati et al., 2002	(d)
$\Phi\{I(^2P_{1/2})\} = 0.50$	236		
$\Phi\{I(^2P_{1/2})\} = 0.50$	266		
$\Phi\{I(^2P_{1/2})\} = 0.55$	280		
$\Phi\{Cl(^2P_{1/2})\} = 0.34$	304	Senapati and Das, 2004	(e)
$\Phi\{Cl(^2P_{1/2})\} = 0.44$	222		
$\Phi\{Cl(^2P_{1/2})\} = 0.44$	266		
$\Phi\{Cl(^2P_{1/2})\} = 0.30$	280		
$\Phi\{Cl(^2P_{1/2})\} = 0.22$	304		

Comments

(a) Absorption coefficients for CH_2CII (purity 98%) were determined by diode array spectrometry with a spectral resolution of 0.6 nm. A single absorption band was observed to extend from 230–400 nm with a maximum at 270 nm where the absorption coefficient was $\sigma = (1.21 \pm 0.07) \times 10^{-18}$ cm^2 molecule^{-1} at 298 K. The temperature dependence of the absorption cross section was determined over the range 243-333 K; broadening of the band was observed giving a significant decline in σ with decreasing temperature in the tropospheric photolysis region ($\lambda > 290$ nm).

(b) The absorption spectrum of CH_2ClI (purity 97%) was recorded by by diode array spectrometry with a resolution of 0.3 nm. The absolute cross section at the maximum of absorption at 270 nm was $\sigma = 1.35 \times 10^{-18}$ cm^2 molecule^{-1} with a stated overall uncertainty of ± 5%. Significance temperature dependence of the absorption cross section was observed over the range 228-298 K, with a decrease in σ with a decrease in temperature in the long wavelength tail. A second absorption band is indicated by an increase in σ below 220 nm.

(c) Laser photolysis of CH_2ClI; measurement of yield of I_2 by time resolved laser absorption spectroscopy at 514.5 nm.

(d) Laser Photolysis-REMPI detection of $I(^2P_{1/2})$ and $I(^2P_{3/2})$.

(e) Laser Photolysis-REMPI detection of $Cl(^2P_{1/2})$ and $Cl(^2P_{3/2})$. Φ determined relative to $\Phi\{I(^2P_{1/2})\}$ production at the same wavelength.

Preferred Values

Absorption cross-sections of CH_2ClI at 298 K

Wavelength/nm	$10^{20}\ \sigma$/cm^2	$10^3\ B$/K^{-1}
205	122	
210	39.1	
215	10.3	
220	7.0	
225	9.06	
230	13.8	
235	21.2	0.24
240	31.8	0.122
245	45.6	-0.018
250	62.9	-0.114
255	84	-0.283
260	105	-0.444
265	121	-0.547
270	127	-0.587
275	120	-0.47
280	103	-0.18
285	80.7	0.317
290	58.1	0.985
295	39.8	1.73
300	25.9	2.56
305	16.7	3.08
310	10.9	3.5
315	7.16	3.56
320	4.79	3.46
325	3.23	3.44
330	2.14	3.72
335	1.4	4.09
340	0.905	4.87
345	0.569	5.69
350	0.35	6.88
355	0.225	8.16
360	0.138	9.01
365	0.081	11.1
370	0.048	11.5
375	0.027	12.8
380	0.017	15.1
385	0.008	19.1
390	0.006	20.5

Temperature dependence given by: $\ln \sigma = \ln \sigma(298) + B(T\text{-}298/\text{K})$

Quantum Yield

$\Phi_1 + \Phi_2 = 1.0$ over the wavelength range 230–390 nm; no recommendation for Φ_2/Φ_1

Comments on Preferred Values

The data of Rattigan et al. (1997) and Roehl et al. (1997) are in excellent agreement both in terms of the absolute absorption cross sections, and their temperature dependence as a function of wavelength. The earlier data of Schmitt and Comes (1987) also showed a maximum at 270 nm but the absolute cross section was higher (1.5×10^{-18} cm^2 $molecule^{-1}$). The preferred values for the cross-sections are a simple mean of data of Rattigan et al. (1997) and Roehl et al. (1997), and the temperature dependence, expressed in terms of a single parameter B in the equation: $\ln \sigma = \ln \sigma(298) + B(T - 298/K)$ from the work of Rattigan et al. (1997) is adopted.

The photodecomposition of CH_2ClI studied by Schmitt and Comes (1987) indicated dissociation via reaction (1), in line with other alkyl iodides, occurring with a quantum yield of unity. The quantum yield of $I(^2P_{1/2})$ are reported by Senapati et al., (2002), who observed a similar trend with wavelength as that observed for photolysis of CH_3I. This suggests that the photodissociation occurs from 3 upper states similar to methyl iodide. However, Senapati and Das 2004 observed $Cl(^2P_{1/2})$ production and measured yields (relative to $I(^2P_{1/2})$), which decrease with increasing wavelength in the range $222 \leq \lambda \leq 304$ nm. An inter-chromophore energy transfer mechanism between C-I and C-Cl chromophore is proposed to rationalise $Cl(^2P_{1/2})$ production.

On the basis of available data it is not possible to recommend a branching ratio for Cl atom formation, but I atom production will predominate in tropospheric photolysis.

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$CH_2BrI + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CH_2BrI + h\nu$	$\rightarrow CH_2Br + I$	(1)	214	559
	$\rightarrow CH_2I + Br$	(2)	280	427
	$\rightarrow CH_2 + IBr$	(3)	369	324

Absorption cross-section data

Wavelength range/nm	Reference	Comments
215–390	Mossinger et al., 1998	(a)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\Phi_1/\Phi_2 = 6$	240-340	Lee and Bersohn, 1982	(b)
$\Phi_1/\Phi_2 = 6$	248	Butler et al., 1987	(c)

Comments

(a) Absorption coefficients for CH_2BrI (purity 98%) were determined by diode array spectrometry with a spectral resolution of 0.6 nm. The purity of the CH_2BrI sample was 92%, the main imputities being CH_2Br_2 (6.5%) and CH_2I_2 1.5%). A correction was applied for absorption by these impurities using spectra obtained in the same spectrometer. Tabulated cross section values for the indicated range were given. Two broad absorption bands attributed to CH_2BrI were observed with maxima at 215nm and 270 nm where the absorption cross sections were $\sigma = (5.67\pm0.34) \times 10^{-18}$ cm^2 molecule^{-1} and $\sigma = (2.34\pm0.14) \times 10^{-18}$ cm^2 molecule^{-1} respectively at 298 K. The temperature dependence of the absorption cross section was determined over the range 273-348 K; broadening of both bands was observed giving a significant decline in σ with decreasing temperature in the tropospheric photolysis region ($\lambda > 290$ nm).

(b) Photodissociation of CH_2BrI with broadband light source; dissociation fragments measured by mass spectrometry. Branching ratio for C-I and C-Br bond fission reported. These workers also reported a UV spectrum.

(c) Product state distributions measured for laser photodissociation CH_2BrI at 193.3, 210, and 248.5 nm of in a molecular beam, using TOF-MS. At 248.5 nm both C-I and C-Br bond fission occurs, with I formation dominant, producing ground state $^2P_{3/2}$ and excited state $^2P_{1/2}$ atoms in ratio of 1.0:0.75. At shorter wavelengths elimination of IBr was also observed.

Preferred Values

Absorption cross-sections of CH_2BrI at 298 K

Wavelength/nm	$10^{20}\ \sigma/\text{cm}^2$	$10^3\ B/\text{K}^{-1}$
215	567	-2.16
220	423	-0.12
225	269	1.34
230	155	2.06
235	97.9	2.05
240	80.9	1.01
245	93.7	0.0
250	125	-0.58
255	170	-1.16
260	207	-1.29
265	228	-1.45
270	229	-1.73
275	214	-1.22
280	184	-0.94
285	150	-0.53
290	110	0.1
295	82.5	0.63
300	60.6	1.03
305	42.9	1.13
310	31.4	1.41
315	23.1	1.52
320	16.8	1.71
325	11.5	2.36
330	8.02	2.99
335	5.52	3.89
340	3.50	4.79
345	2.24	5.74
350	1.41	6.73
355	0.817	9.47
360	0.498	11.5
365	0.302	11.6
370	0.165	14.3
375	0.098	17.4
380	0.070	
385	0.039	
390	0.025	

Temperature dependence given by: $\ln \sigma = \ln \sigma(298) + B(T\text{-}298/\text{K})$

Quantum Yield

$\Phi_1 = 1.0$ over the wavelength range 290–380 nm.

Comments on Preferred Values

The preferred values for the cross sections and the temperature dependence are those of Mössinger et al. (1998), which appears to be the only reported study where absolute cross section were reported. Cross sections obtained for other halocarbons by this group agree well with other literature data and the CH_2BrI data can be considered reliable. The absorption spectrum agrees with earlier reported spectra (Lee and R. Bersohn, 1982; Butler et al., 1987), which show two broad bands peaking at 270 nm and 215 nm which are assigned to promotion of electrons from non-bonding orbitals in the C-I and C-Br bonds respectively.

The photodissociation of CH_2BrI via reaction (1) is expected to occur in the first absorption band with a quantum yield of unity, in line with other alkyl iodides. Studies of the photodissociation fragments (Lee and Bersohn, 1982) show that reaction (2) is dominant following absorption in the second band at 210 nm and that both processes occur in the region where the bands overlap. In the region for tropospheric photolysis ($\lambda > 290$ nm) reaction (1) will dominate.

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$CH_2I_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CH_2I_2 + h\nu$	$\rightarrow CH_2I + I$	(1)	219	547
	$\rightarrow CH_2 + I_2$	(2)	335	357

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–360	Schmitt and Comes, 1980	(a)
265–340	Koffend and Leone, 1981	(b)
200–380	Roehl et al., 1997	(c)
200–380	Mössinger et al., 1998	(d)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\Phi(I_2)$	300	Schmitt and Comes, 1980	(e)
$\Phi\{I(^2P_{1/2}; I(^2P_{3/2})\}$	254	Baughcum and Leone, 1980	(f)
$\Phi\{I(^2P_{1/2})\}$	248-340	Koffend and Leone, 1981	(g)

Comments

(a) Conventional UV absorption spectrometry. The spectrum consisted of two asymmetrical peaks at 288 nm and 248 nm, suggesting several overlapping bands, and a third band below 220 nm. The absolute cross-section at the first maximum of absorption at 290 nm was $\sigma = 4.07 \times 10^{-18}$ cm^2 molecule^{-1}.

(b) The absorption spectrum of CH_2I_2 was recorded by conventional UV absorption spectrometry. The absolute cross-section at the first maximum of absorption at 286 nm was $\sigma = 3.92 \times 10^{-18}$ cm^2 molecule^{-1}.

(c) The absorption spectrum of CH_2I_2 (purity 97%) was recorded by diode array spectrometry with a resolution of 0.3 nm. The third absorption maximum occured at 210 nm. The absolute cross-section at the first maximum of absorption at 290 nm was $\sigma = 3.84 \times 10^{-18}$ cm^2 molecule^{-1} with a stated overall uncertainty of ±5%. This was within 6% of the value of Schmitt and Comes (1980) and 2% of the Koffend and Leone data (1981). Significant temperature dependence of the absorption cross section was observed over the range 273–298K, with a decrease in σ with decreasing temperature in the long wavelength tail.

(d) Absorption coefficients for CH_2I_2 (purity 98%) were determined by diode array spectrometry with a spectral resolution of 0.6 nm. Tabulated cross section values for the indicated range were given. The absolute cross-sections at absorption maxima of 248 nm and 288 nm were $\sigma = (1.62\pm0.10) \times 10^{-18}$ cm^2 molecule^{-1} and $\sigma = (3.78\pm0.23) \times 10^{-18}$ cm^2 molecule^{-1}, respectively, at 298 K. The temperature dependence of the absorption cross section was determined over the range 278-348 K; the temperature dependence was complex reflecting the presence of several overlapping bands but there was a significant decline in σ with decreasing temperature in the tropospheric photolysis region ($\lambda > 290$ nm).

(e) Pulsed laser photolysis of CH_2I_2; measurement of yield of I_2 by absorption spectrometry. Primary products deduced to be I atoms, partially in the excited state.

(f) Pulsed tunable laser photolysis of CH_2I_2, with $I(^2P_{1/2})$ and excited CH_2I_2 detection by infra red emission.

(g) Pulsed tunable laser photolysis of CH_2I_2, with $I(^2P_{1/2})$ detection by infra red fluorescence at 1.315 μm. $\Phi\{I(^2P_{1/2})\}$ increased from zero to 0.46 over the wavelength range 340 – 248 nm.

Preferred Values

Absorption cross-sections of CH_2I_2 at 298 K

Wavelength/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	$10^3\ B/\mathrm{K}^{-1}$
205	407	
210	404	
215	322	0.1515
220	260	0.14
225	198	0.19
230	132	0.51
235	109	0.56
240	123	0.15
245	150	0.18
250	157	0.67
255	140	1.58
260	120	2.04
265	130	1.30
270	179	0
275	255	-0.71
280	328	-1.24
285	373	-1.21
290	381	-0.94
295	372	-0.58
300	357	-0.37
305	338	0
310	314	0.07
315	280	0.15
320	244	0.27
325	203	0.27
330	161	0.51
335	120	0.55
340	83.3	1.36
345	53.7	1.99
350	32.6	3.19
355	19.2	4.09
360	10.9	5.39
365	6.05	6.77
370	3.4	8.25
375	1.93	11.3
380	1.16	
385	0.77	

Temperature dependence given by: $\ln\sigma = \ln\sigma(298) + B(T\text{-}298/\mathrm{K})$

Quantum Yield

$\Phi_1 = 1.0$ over the wavelength range 230–380 nm.

Comments on Preferred Values

There is good agreement between all the reported absorption spectra of CH_2I_2. The cross section data of Roehl et al. (1997) and Mössinger et al. (1998) are in excellent agreement both in terms of the absolute absorption cross sections, and its temperature dependence as a function of wavelength, expressed in terms of a single parameter B in the equation $\ln \sigma = \ln \sigma(298) + B(T\text{-}298/\mathrm{K})$. The preferred values for the cross-sections are a simple mean from both data sets, and the temperature dependence of Mössinger et al. (1998) is adopted since it is based on a wider range of temperature.

The study of the photodecomposition of CH_2I_2 by Schmitt and Comes (1980) indicated dissociation via reaction (1), in line with other alkyl iodides, occurring with a quantum yield of unity. Reaction (2) may be important following absorption in the band centered at λ = 215 nm. A significant fraction of I atoms are formed in the excited state in the tropospheric photolysis of CH_2I_2.

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