

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

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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. 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 In 1986 the IUPAC Subcommittee on Data Evaluation superseded the original CODATA Task Group for Atmospheric Chemistry, and the Subcommittee has continued its data evaluation program with Supplements published in 1989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

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as individual PDF or word files. In order to further enhance the accessibility of this updated material to the scientific community, the evaluation is being published as a series of articles in Atmospheric Chemistry and Physics. This article is the fourth of the series, Volume IV.

## 5 **Summary of recommended rate coefficients for organic halogen reactions**

The ordering of families in the Summary Table is:  $\text{FO}_x$  (Appendix 1),  $\text{ClO}_x$  (Appendix 2),  $\text{BrO}_x$  (Appendix 3) and  $\text{IO}_x$  (Appendix 4). The reactions are numbered sequentially for the whole Volume. Within each family, reactions are listed in the order:  $\text{O}(^3\text{P})$ ,  $\text{O}(^1\text{D})$ , halogen atom, HO radical,  $\text{NO}_3$  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.

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

Reaction number	Reaction	$k_{298}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/K^a$
<i>FO<sub>x</sub> Reactions - based on data sheets in Appendix 1, and on the IUPAC website updated in 2005.</i>						
1	O( <sup>1</sup> D)+COF <sub>2</sub> → O( <sup>3</sup> P)+COF <sub>2</sub> → other products	5.2×10 <sup>-11</sup> 2.2×10 <sup>-11</sup>				
	<b>overall</b>	7.4×10 <sup>-11</sup>	±0.3			
2	O( <sup>1</sup> D)+CH <sub>3</sub> F → O( <sup>3</sup> P)+CH <sub>3</sub> F → other products	2.7×10 <sup>-11</sup> 1.2×10 <sup>-10</sup>				
	<b>overall</b>	1.5×10 <sup>-10</sup>	±0.15			
3	O( <sup>1</sup> D)+CH <sub>2</sub> F <sub>2</sub> → O( <sup>3</sup> P)+CH <sub>2</sub> F <sub>2</sub> → other products	3.6×10 <sup>-11</sup> 1.5×10 <sup>-11</sup>				
	<b>overall</b>	5.1×10 <sup>-11</sup>	±0.3			
4	O( <sup>1</sup> D)+CHF <sub>3</sub> → O( <sup>3</sup> P)+CHF <sub>3</sub> → other products	8.2×10 <sup>-12</sup> 9.1×10 <sup>-13</sup>				
	<b>overall</b>	9.1×10 <sup>-12</sup>	±0.15			
5	O( <sup>1</sup> D)+CH <sub>3</sub> CH <sub>2</sub> F → O( <sup>3</sup> P)+CH <sub>3</sub> CH <sub>2</sub> F → other products	4.7×10 <sup>-11</sup> 2.1×10 <sup>-10</sup>				
	<b>overall</b>	2.6×10 <sup>-10</sup>	±0.3			
6	O( <sup>1</sup> D)+CH <sub>3</sub> CHF <sub>2</sub> → O( <sup>3</sup> P)+CH <sub>3</sub> CHF <sub>2</sub> → other products	1.1×10 <sup>-10</sup> 9.2×10 <sup>-11</sup>				
	<b>overall</b>	2.0×10 <sup>-10</sup>	±0.3			
7	O( <sup>1</sup> D)+CH <sub>3</sub> CF <sub>3</sub> → O( <sup>3</sup> P)+CH <sub>3</sub> CF <sub>3</sub> → other products	5.8×10 <sup>-11</sup>	±0.5			
8	O( <sup>1</sup> D)+CH <sub>2</sub> FCF <sub>3</sub> → O( <sup>3</sup> P)+CH <sub>2</sub> FCF <sub>3</sub> → other products	4.6×10 <sup>-11</sup> 3.0×10 <sup>-12</sup>				
	<b>overall</b>	4.9×10 <sup>-11</sup>	±0.3			

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Reaction number	Reaction	$k_{298}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$\Delta \log k_{298}^a$	Temp. dependence of $k$ /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp. range/K	$\Delta(E/R)/K^a$
9	O( <sup>1</sup> D)+CHF <sub>2</sub> CF <sub>3</sub> → O( <sup>3</sup> P)+CHF <sub>2</sub> CF <sub>3</sub> → other products	1.0×10 <sup>-10</sup> 1.8×10 <sup>-11</sup>				
	<b>overall</b>	1.2×10 <sup>-10</sup>	±0.3			
10	HO+CH <sub>3</sub> F → H <sub>2</sub> O+CH <sub>2</sub> F	2.1×10 <sup>-14</sup>	±0.15	1.9×10 <sup>-12</sup> exp(-1350/T)	240–300	±400
11	HO+CH <sub>2</sub> F <sub>2</sub> → H <sub>2</sub> O+CHF <sub>2</sub>	1.1×10 <sup>-14</sup>	±0.10	2.3×10 <sup>-12</sup> exp(-1590/T)	220–300	±200
12	HO+CHF <sub>3</sub> → H <sub>2</sub> O+CF <sub>3</sub>	2.7×10 <sup>-16</sup>	±0.2	6.9×10 <sup>-13</sup> exp(-2340/T)	250–300	±300
13	HO+CF <sub>4</sub> → HOF+CF <sub>3</sub>	<2×10 <sup>-18</sup>				
14	HO+CH <sub>3</sub> CH <sub>2</sub> F → H <sub>2</sub> O+CH <sub>3</sub> CHF → H <sub>2</sub> O+CH <sub>2</sub> CH <sub>2</sub> F	1.8×10 <sup>-13</sup> 3.2×10 <sup>-14</sup>				
	<b>overall</b>	2.1×10 <sup>-13</sup>	±0.2	2.7 × 10 <sup>-12</sup> exp(-765/T)	210–300	±300
15	HO+CH <sub>3</sub> CHF <sub>2</sub> → H <sub>2</sub> O+CH <sub>2</sub> CHF <sub>2</sub> → H <sub>2</sub> O+CH <sub>3</sub> CF <sub>2</sub>					
	<b>overall</b>	3.6×10 <sup>-14</sup>	+0.10 -0.20	1.25×10 <sup>-12</sup> exp(-1070/T)	210–300	+200 -400
16	HO+CH <sub>3</sub> CF <sub>3</sub> → H <sub>2</sub> O+CH <sub>2</sub> CF <sub>3</sub>	1.2 × 10 <sup>-15</sup>	±0.15	9.2×10 <sup>-13</sup> exp(-1970/T)	220–300	±300
17	HO+CH <sub>2</sub> FCH <sub>2</sub> F → H <sub>2</sub> O+CH <sub>2</sub> FCHF	1.0 × 10 <sup>-13</sup>	±0.3	1.5×10 <sup>-12</sup> exp(-800/T)	210–300	±200
18	HO+CH <sub>2</sub> FCHF <sub>2</sub> → H <sub>2</sub> O+CH <sub>2</sub> FCF <sub>2</sub> → H <sub>2</sub> O+CHFCHF <sub>2</sub>					
	<b>overall</b>	1.5×10 <sup>-14</sup>	±0.2	3.3 × 10 <sup>-12</sup> exp(-1610/T)	270–330	±300
19	HO+CH <sub>2</sub> FCF <sub>3</sub> → H <sub>2</sub> O+CHFCF <sub>3</sub>	4.6×10 <sup>-15</sup>	±0.2	4.9×10 <sup>-13</sup> exp(-1395/T)	220–300	±300
20	HO+CHF <sub>2</sub> CHF <sub>2</sub> → H <sub>2</sub> O+CF <sub>2</sub> CHF <sub>2</sub>	6.1 × 10 <sup>-15</sup>	±0.2	1.4×10 <sup>-12</sup> exp(-1620/T)	290–360	±300
21	HO+CHF <sub>2</sub> CF <sub>3</sub> → H <sub>2</sub> O+CF <sub>2</sub> CF <sub>3</sub>	1.9 × 10 <sup>-15</sup>	±0.2	4.4×10 <sup>-13</sup> exp(-1630/T)	220–300	±300
22	HO+CHF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> F → H <sub>2</sub> O+CHF <sub>2</sub> CF <sub>2</sub> CHF → H <sub>2</sub> O+CF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> F					
	<b>overall</b>	7.7×10 <sup>-15</sup>	±0.3	2.2 × 10 <sup>-12</sup> exp(-1685/T)	285–365	±300
23	HO+CF <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> F → H <sub>2</sub> O+CF <sub>3</sub> CF <sub>2</sub> CHF	6.5×10 <sup>-15</sup>	±0.3	2.6 × 10 <sup>-13</sup> exp(-1100/T)	250–320	±400

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24	$\text{HO} + \text{CF}_3\text{CHFCHF}_2 \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CFCHF}_2$ $\rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CHFCHF}_2$					
	<b>overall</b>	$5.0 \times 10^{-15}$	$\pm 0.3$	$1.4 \times 10^{-12} \exp(-1680/T)$	290–380	$\pm 300$
25	$\text{HO} + \text{CF}_3\text{CH}_2\text{CF}_3 \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CHCF}_3$	$3.3 \times 10^{-16}$	$\pm 0.3$	$1.3 \times 10^{-12} \exp(-2465/T)$	270–340	$\pm 400$
26	$\text{HO} + \text{CF}_3\text{CHFCF}_3 \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CFCF}_3$	$1.4 \times 10^{-15}$	$\pm 0.2$	$5.3 \times 10^{-13} \exp(-1770/T)$	250–380	$\pm 300$
27	$\text{HO} + \text{CHF}_2\text{OCHF}_2 \rightarrow \text{H}_2\text{O} + \text{CHF}_2\text{OCF}_2$	$2.2 \times 10^{-15}$	$\pm 0.1$	$1.9 \times 10^{-12} \exp(-2020/T)$	270–460	$\pm 300$
28	$\text{HO} + \text{HCOF} \rightarrow \text{H}_2\text{O} + \text{FCO}$	$< 1 \times 10^{-14}$				
29	$\text{HO} + \text{CHF}_2\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CHF}_2\text{CO}$ $\rightarrow \text{H}_2\text{O} + \text{CF}_2\text{CHO}$					
	<b>overall</b>	$1.6 \times 10^{-12}$	$\pm 0.2$			
30	$\text{HO} + \text{CF}_3\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CO}$	$5.8 \times 10^{-13}$	$\pm 0.2$			
31	$\text{HO} + \text{CF}_3\text{COOH} \rightarrow \text{products}$	$1.3 \times 10^{-13}$	$\pm 0.1$	$1.3 \times 10^{-13}$	280–350	$\Delta \log k = \pm 0.1$
32	$\text{HO}_2 + \text{CH}_2\text{FO}_2 \rightarrow \text{O}_2 + \text{CH}_2\text{FO}_2\text{H}$ $\rightarrow \text{O}_2 + \text{HCOF} + \text{H}_2\text{O}$	See data sheet				
33	$\text{HO}_2 + \text{CF}_3\text{O}_2 \rightarrow \text{CF}_3\text{O}_2\text{H} + \text{O}_2$ $\rightarrow \text{C(O)F}_2 + \text{HOF} + \text{O}_2$	no recommendation				
34	$\text{HO}_2 + \text{CF}_3\text{CHFO}_2 \rightarrow \text{O}_2 + \text{CF}_3\text{CHFO}_2\text{H}$ $\rightarrow \text{O}_2 + \text{CF}_3\text{C(O)F} + \text{H}_2\text{O}$	$4.3 \times 10^{-12}$	$\pm 0.2$			
	<b>overall</b>	$4.3 \times 10^{-12}$	$\pm 0.2$	$2.0 \times 10^{-13} \exp(910/T)$	210–365	$\pm 300$
35	$\text{HO}_2 + \text{CF}_3\text{CF}_2\text{O}_2 \rightarrow \text{O}_2 + \text{CF}_3\text{CF}_2\text{O}_2\text{H}$ $\rightarrow \text{O}_2 + \text{CF}_3\text{C(O)F} + \text{HOF}$					
	<b>overall</b>	$1.2 \times 10^{-12}$	$\pm 0.5$			
36	$\text{FO}_2 + \text{CO} \rightarrow \text{products}$	$< 6 \times 10^{-16}$				
37	$\text{FO}_2 + \text{CH}_4 \rightarrow \text{products}$	$< 4.1 \times 10^{-15}$				

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38	$\text{CF}_3 + \text{O}_2 + \text{M} \rightarrow \text{CF}_3\text{O}_2 + \text{M}$	$2.2 \times 10^{-29} [\text{N}_2]$ $4 \times 10^{-12}$ $F_c = 0.39$	$(k_0) \pm 0.1$ $(k_\infty) \pm 0.3$	$2.2 \times 10^{-29} (T/300)^{-4.7} [\text{N}_2]$ $4 \times 10^{-12}$ $F_c = 0.39$	230–380 200–300	$\Delta n = \pm 1.5$ $\Delta n = \pm 1.5$
39	$\text{CF}_3\text{O} + \text{O}_2 \rightarrow \text{COF}_2 + \text{FO}_2$	$< 1 \times 10^{-18}$		$< 1 \times 10^{-10} \exp(-5600/T)$	250–370	
40	$\text{CF}_3\text{O} + \text{O}_3 \rightarrow \text{CF}_3\text{O}_2 + \text{O}_2$	$1.8 \times 10^{-14}$	$\pm 1$	$2 \times 10^{-12} \exp(-1400/T)$	250–370	$\pm 600$
41	$\text{CF}_3\text{O} + \text{H}_2\text{O} \rightarrow \text{CF}_3\text{OH} + \text{HO}$	$< 2 \times 10^{-17}$		$< 3 \times 10^{-12} \exp(-3600/T)$	250–380	
42	$\text{CF}_3\text{O} + \text{NO} \rightarrow \text{COF}_2 + \text{FNO}$	$5.4 \times 10^{-11}$	$\pm 0.1$	$3.7 \times 10^{-11} \exp(110/T)$	230–390	$\pm 100$
43	$\text{CF}_3\text{O} + \text{CH}_4 \rightarrow \text{CF}_3\text{OH} + \text{CH}_3$	$2.2 \times 10^{-14}$	$\pm 0.1$	$2.6 \times 10^{-12} \exp(-1420/T)$	230–380	$\pm 200$
44	$\text{CF}_3\text{O} + \text{C}_2\text{H}_6 \rightarrow \text{CF}_3\text{OH} + \text{C}_2\text{H}_5$	$1.3 \times 10^{-12}$	$\pm 0.1$	$4.9 \times 10^{-12} \exp(-400/T)$	230–360	$\pm 200$
45	$\text{CH}_2\text{FO} + \text{O}_2 \rightarrow \text{HCOF} + \text{HO}_2$			See data sheet		
46	$\text{CH}_2\text{FO} + \text{M} \rightarrow \text{HCOF} + \text{H} + \text{M}$			See data sheet		
47	$\text{CH}_3\text{CF}_2\text{O} + \text{O}_2 \rightarrow \text{products}$			See data sheet		
48	$\text{CH}_3\text{CF}_2\text{O} + \text{M} \rightarrow \text{CH}_3 + \text{COF}_2 + \text{M}$			See data sheet		
49	$\text{CH}_2\text{FCHFO} + \text{O}_2 \rightarrow \text{CH}_2\text{FCOF} + \text{HO}_2$			See data sheet		
50	$\text{CH}_2\text{FCHFO} + \text{M} \rightarrow \text{CH}_2\text{F} + \text{HCOF} + \text{M}$			See data sheet		
51	$\text{CF}_3\text{CHFO} + \text{O}_2 \rightarrow \text{CF}_3\text{COF} + \text{HO}_2$			See data sheet		
52	$\text{CF}_3\text{CHFO} + \text{M} \rightarrow \text{CF}_3 + \text{HCOF} + \text{M}$			See data sheet		
53	$\text{CF}_3\text{CF}_2\text{O} + \text{O}_2 \rightarrow \text{products}$			See data sheet		
54	$\text{CF}_3\text{CF}_2\text{O} + \text{M} \rightarrow \text{CF}_3 + \text{CF}_2\text{O} + \text{M}$			See data sheet		
55	$\text{CH}_2\text{FO}_2 + \text{NO} \rightarrow \text{CH}_2\text{FO} + \text{NO}_2$	$1.3 \times 10^{-11}$	$\pm 0.3$			
56	$\text{CHF}_2\text{O}_2 + \text{NO} \rightarrow \text{CHF}_2\text{O} + \text{NO}_2$	$1.3 \times 10^{-11}$	$\pm 0.3$			
57	$\text{CF}_3\text{O}_2 + \text{NO} \rightarrow \text{CF}_3\text{O} + \text{NO}_2$	$1.6 \times 10^{-11}$	$\pm 0.1$	$1.6 \times 10^{-11} \exp(T/298)^{-1.2}$	230–430	$\Delta n = \pm 0.5$
58	$\text{CH}_2\text{FCHFO}_2 + \text{NO}$ $\rightarrow \text{CH}_2\text{FCHFO} + \text{NO}_2$	$> 9 \times 10^{-12}$				
59	$\text{CHF}_2\text{CF}_2\text{O}_2 + \text{NO} \rightarrow \text{CHF}_2\text{CF}_2\text{O} + \text{NO}_2$	$> 1 \times 10^{-11}$				

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60	$\text{CF}_3\text{CHFO}_2 + \text{NO} \rightarrow \text{CF}_3\text{CHFO} + \text{NO}_2$	$1.3 \times 10^{-11}$	$\pm 0.2$			
61	$\text{CF}_3\text{CF}_2\text{O}_2 + \text{NO} \rightarrow \text{CF}_3\text{CF}_2\text{O} + \text{NO}_2$	$> 1 \times 10^{-11}$				
62	$\text{CF}_3\text{O}_2 + \text{NO}_2 + \text{M} \rightarrow \text{CF}_3\text{O}_2\text{NO}_2 + \text{M}$	$5.6 \times 10^{-29} [\text{N}_2]$	$(k_0) \pm 0.2$	$5.6 \times 10^{-29} (T/298)^{-9} [\text{N}_2]$	260–300	$\Delta n = \pm 3$
		$7.7 \times 10^{-12}$	$(k_\infty) \pm 0.2$	$7.7 \times 10^{-12} (T/298)^{-0.67}$	260–300	$\Delta n = \pm 0.5$
		$F_c = 0.31$		$F_c = 0.31$	260–300	
63	$\text{CF}_3\text{O}_2\text{NO}_2 + \text{M} \rightarrow \text{CF}_3\text{O}_2 + \text{NO}_2 + \text{M}$	$4.5 \times 10^{-19} [\text{N}_2]$	$(k_0/\text{s}^{-1}) \pm 0.3$	$2.5 \times 10^{-5} \exp(-9430/T) [\text{N}_2]$	260–300	$\pm 250$
		$6.0 \times 10^{-2}$	$(k_\infty/\text{s}^{-1}) \pm 0.3$	$1.5 \times 10^{16} \exp(-11940/T)$	260–300	$\pm 250$
		$F_c = 0.31$		$F_c = 0.31$	260–300	
64	$\text{CH}_2\text{FO}_2 + \text{CH}_2\text{FO}_2$ $\rightarrow \text{CH}_2\text{FOH} + \text{C}(\text{O})\text{F} + \text{O}_2$ $\rightarrow 2\text{CH}_2\text{FO} + \text{O}_2$					
		$2.6 \times 10^{-12}$	$\pm 0.3$			
		<b>overall</b>	$2.6 \times 10^{-12}$	$\pm 0.3$	$2.5 \times 10^{-13} \exp(700/T)$	220–380 $\pm 300$
65	$\text{CHF}_2\text{O}_2 + \text{CHF}_2\text{O}_2$ $\rightarrow \text{CHF}_2\text{OH} + \text{C}(\text{O})\text{F}_2 + \text{O}_2$ $\rightarrow 2\text{CHF}_2\text{O} + \text{O}_2$					
		See data sheet				
		<b>overall</b>	$(2.5\text{--}5.0) \times 10^{-12}$			
66	$\text{CF}_3\text{O}_2 + \text{CF}_3\text{O}_2 \rightarrow 2\text{CF}_3\text{O} + \text{O}_2$	$1.5 \times 10^{-12}$	$\pm 0.3$			
67	$\text{CF}_3\text{O}_2 + \text{CF}_3\text{CHFO}_2$ $\rightarrow \text{CF}_3\text{OH} + \text{CF}_3\text{COF} + \text{O}_2$ $\rightarrow \text{CF}_3\text{O} + \text{CF}_3\text{CHFO} + \text{O}_2$					
		<b>overall</b>	$8 \times 10^{-12}$	$\pm 0.5$		
68	$\text{CHF}_2\text{CF}_2\text{O}_2 + \text{CHF}_2\text{CF}_2\text{O}_2$ $\rightarrow \text{CHF}_2\text{CF}_2\text{O} + \text{CHF}_2\text{CF}_2\text{O} + \text{O}_2$	no recommendation				

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69	$\text{CF}_3\text{CHFO}_2 + \text{CF}_3\text{CHFO}_2$					
	$\rightarrow \text{CF}_3\text{CHFOH} + \text{CF}_3\text{COF} + \text{O}_2$	$3.3 \times 10^{-13}$				
	$\rightarrow 2 \text{CF}_3\text{CHFO} + \text{O}_2$	$4.4 \times 10^{-12}$				
<b>overall</b>		$4.7 \times 10^{-12}$	$\pm 0.3$	$6.2 \times 10^{-13} \exp(605/T)$	210-375	$\pm 200$
70	$\text{CF}_3\text{CF}_2\text{O}_2 + \text{CF}_3\text{CF}_2\text{O}_2$	no recommendation				
	$\rightarrow 2 \text{CF}_3\text{CF}_2\text{O} + \text{O}_2$					

Data for the following Photochemical Reactions is based on data sheets on the IUPAC website updated in 2005

71	$\text{HC(O)F} + h\nu \rightarrow \text{products}$
72	$\text{C(O)F}_2 + h\nu \rightarrow \text{products}$
73	$\text{CF}_3\text{CHO} + h\nu \rightarrow \text{products}$
74	$\text{CF}_3\text{COF} + h\nu \rightarrow \text{products}$

$\text{ClO}_x$  Reactions - based on data sheets in Appendix 2, and on the IUPAC website updated in 2005

75	$\text{O}(^1\text{D}) + \text{CHF}_2\text{Cl} \rightarrow \text{O}(^3\text{P}) + \text{CHF}_2\text{Cl}$	$2.8 \times 10^{-11}$				
	$\rightarrow \text{ClO} + \text{CHF}_2$	$5.5 \times 10^{-11}$				
	$\rightarrow \text{other products}$	$1.7 \times 10^{-11}$				
	<b>overall</b>	$1.0 \times 10^{-10}$	$\pm 0.1$	$1 \times 10^{-10}$	170-350	$\Delta \log k = \pm 0.1$
76	$\text{O}(^1\text{D}) + \text{CHFCl}_2 \rightarrow \text{ClO} + \text{CHFCl}$	$1.4 \times 10^{-10}$				
	$\rightarrow \text{other products}$	$5.0 \times 10^{-11}$				
	<b>overall</b>	$1.9 \times 10^{-10}$	$\pm 0.3$	$1.9 \times 10^{-10}$	180-350	$\Delta \log k = \pm 0.3$
77	$\text{O}(^1\text{D}) + \text{CH}_3\text{CF}_2\text{Cl} \rightarrow \text{O}(^3\text{P}) + \text{CH}_3\text{CF}_2\text{Cl}$	$5.7 \times 10^{-11}$				
	$\rightarrow \text{other products}$	$1.6 \times 10^{-10}$				
	<b>overall</b>	$2.2 \times 10^{-10}$	$\pm 0.3$			

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Reaction number	Reaction	$k_{298}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta (E/R)/\text{K}^a$
78	$\text{O}(^1\text{D}) + \text{CH}_3\text{CFCl}_2 \rightarrow \text{O}(^3\text{P}) + \text{CH}_3\text{CFCl}_2$ → other products	$8.1 \times 10^{-11}$ $1.8 \times 10^{-10}$				
	<b>overall</b>	$2.6 \times 10^{-10}$	$\pm 0.3$			
79	$\text{O}(^1\text{D}) + \text{CH}_2\text{ClCF}_3 \rightarrow \text{O}(^3\text{P}) + \text{CH}_2\text{ClCF}_3$ → other products	$2.4 \times 10^{-11}$ $9.6 \times 10^{-11}$				
	<b>overall</b>	$1.2 \times 10^{-10}$	$\pm 0.3$			
80	$\text{O}(^1\text{D}) + \text{CH}_2\text{ClCF}_2\text{Cl} \rightarrow \text{O}(^3\text{P}) + \text{CH}_2\text{ClCF}_2\text{Cl}$ → other products	$1.6 \times 10^{-10}$	$\pm 0.5$			
81	$\text{O}(^1\text{D}) + \text{CHFClCF}_3 \rightarrow \text{O}(^3\text{P}) + \text{CHFClCF}_3$ → other products	$2.7 \times 10^{-11}$ $5.9 \times 10^{-11}$				
	<b>overall</b>	$8.6 \times 10^{-11}$	$\pm 0.3$			
82	$\text{O}(^1\text{D}) + \text{CHCl}_2\text{CF}_3 \rightarrow \text{O}(^3\text{P}) + \text{CHCl}_2\text{CF}_3$ → other products	$4.2 \times 10^{-11}$ $1.6 \times 10^{-10}$				
	<b>overall</b>	$2.0 \times 10^{-10}$	$\pm 0.3$			
83	$\text{O}(^1\text{D}) + \text{CF}_2\text{Cl}_2 \rightarrow \text{ClO} + \text{CF}_2\text{Cl}$ → $\text{O}(^3\text{P}) + \text{CF}_2\text{Cl}_2$	$1.2 \times 10^{-10}$ $2.4 \times 10^{-11}$				
	<b>overall</b>	$1.4 \times 10^{-10}$	$\pm 0.1$	$1.4 \times 10^{-10}$	170-350	$\Delta \log k = \pm 0.1$
84	$\text{O}(^1\text{D}) + \text{CFCl}_3 \rightarrow \text{ClO} + \text{CFCl}_2$ → $\text{O}(^3\text{P}) + \text{CFCl}_3$	$2.0 \times 10^{-10}$ $3.0 \times 10^{-11}$				
	<b>overall</b>	$2.3 \times 10^{-10}$	$\pm 0.1$	$2.3 \times 10^{-10}$	170-350	$\Delta \log k = \pm 0.1$
85	$\text{O}(^1\text{D}) + \text{CCl}_4 \rightarrow \text{ClO} + \text{CCl}_3$ → $\text{O}(^3\text{P}) + \text{CCl}_4$	$2.9 \times 10^{-10}$ $4.0 \times 10^{-11}$				
	<b>overall</b>	$3.3 \times 10^{-10}$	$\pm 0.1$	$3.3 \times 10^{-10}$	200-350	$\Delta \log k = \pm 0.1$
86	$\text{O}(^1\text{D}) + \text{COFCl} \rightarrow \text{O}(^3\text{P}) + \text{COFCl}$	$1.9 \times 10^{-10}$	$\pm 0.3$			

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Reaction number	Reaction	$k_{298}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$\Delta \log k_{298}^a$	Temp. dependence of $k$ /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp. range/K	$\Delta (E/R)/K^a$
87	O( <sup>1</sup> D)+COCl <sub>2</sub> → O( <sup>3</sup> P)+COCl <sub>2</sub> → O( <sup>3</sup> P)+Cl <sub>2</sub> +CO → other products	See data sheet See data sheet 1.8×10 <sup>-10</sup>				
	<b>overall</b>	2.2×10 <sup>-10</sup>	±0.1	2.0×10 <sup>-10</sup> exp(25/ <i>T</i> )	190-430	±25
88	Cl+HC(O)Cl → HCl+ClCO	7.5×10 <sup>-13</sup>	±0.1	8.1×10 <sup>-12</sup> exp(-710/ <i>T</i> )	220-330	±150
89	Cl+CH <sub>3</sub> OCl → Cl <sub>2</sub> +CH <sub>3</sub> O → HCl+CH <sub>2</sub> OCl	5.2×10 <sup>-11</sup> 9.15×10 <sup>-12</sup>				
	<b>overall</b>	6.1×10 <sup>-11</sup>	±0.1			
90	Cl+CH <sub>3</sub> F → HCl+CH <sub>2</sub> F	3.5×10 <sup>-13</sup>	±0.15	4.0×10 <sup>-12</sup> exp(-730/ <i>T</i> )	240-370	±400
91	Cl+CH <sub>3</sub> Cl → HCl+CH <sub>2</sub> Cl	4.8×10 <sup>-13</sup>	±0.1	2.3×10 <sup>-11</sup> exp(-1150/ <i>T</i> )	220-360	±200
92	Cl+CH <sub>2</sub> F <sub>2</sub> → HCl+CHF <sub>2</sub>	5.0×10 <sup>-14</sup>	±0.5	7.0×10 <sup>-12</sup> exp(-1470/ <i>T</i> )	280-370	±500
93	Cl+CH <sub>2</sub> FCl → HCl+CHFCl	1.1×10 <sup>-13</sup>	±0.3	7.0×10 <sup>-12</sup> exp(-1230/ <i>T</i> )	270-370	±500
94	Cl+CH <sub>2</sub> Cl <sub>2</sub> → HCl+CHCl <sub>2</sub>	3.4×10 <sup>-13</sup>	±0.1	5.9×10 <sup>-12</sup> exp(-850/ <i>T</i> )	220-400	±200
95	Cl+CHF <sub>2</sub> Cl → HCl+CF <sub>2</sub> Cl	1.7×10 <sup>-15</sup>	±0.15	5.9×10 <sup>-12</sup> exp(-2430/ <i>T</i> )	290-430	±400
96	Cl+CHFCl <sub>2</sub> → HCl+CFCl <sub>2</sub>	2.0×10 <sup>-14</sup>	±0.2	5.5×10 <sup>-12</sup> exp(-1675/ <i>T</i> )	290-430	±400
97	Cl+CHCl <sub>3</sub> → HCl+CCl <sub>3</sub>	1.1×10 <sup>-13</sup>	±0.2	2.4×10 <sup>-12</sup> exp(-920/ <i>T</i> )	220-500	±400
98	Cl+CH <sub>3</sub> CH <sub>2</sub> F → HCl+CH <sub>3</sub> CHF → HCl+CH <sub>2</sub> CH <sub>2</sub> F	6.5×10 <sup>-12</sup> 7.4×10 <sup>-13</sup>	±0.3 ±0.3	1.0×10 <sup>-11</sup> exp(-130/ <i>T</i> ) 8.3×10 <sup>-12</sup> exp(-720/ <i>T</i> )	280-370 280-370	±500 ±500
99	Cl+CH <sub>3</sub> CHF <sub>2</sub> → HCl+CH <sub>3</sub> CF <sub>2</sub> → HCl+CH <sub>2</sub> CHF <sub>2</sub>	2.5×10 <sup>-13</sup> 2.3×10 <sup>-15</sup>	±0.15 ±0.5	6.3×10 <sup>-12</sup> exp(-965/ <i>T</i> ) 7.0×10 <sup>-12</sup> exp(-2400/ <i>T</i> )	280-360 280-360	±500 ±500
100	Cl+CH <sub>2</sub> FCH <sub>2</sub> F → HCl+CH <sub>2</sub> FCHF	7.0×10 <sup>-13</sup>	±0.2	2.5×10 <sup>-11</sup> exp(-1065/ <i>T</i> )	280-360	±400
101	Cl+CH <sub>3</sub> CF <sub>3</sub> → HCl+CH <sub>2</sub> CF <sub>3</sub>	2.6×10 <sup>-17</sup>	±0.5	6.9×10 <sup>-12</sup> exp(-3720/ <i>T</i> )	280-370	±500
102	Cl+CH <sub>2</sub> FCHF <sub>2</sub> → HCl+CH <sub>2</sub> FCF <sub>2</sub> → HCl+CHFCHF <sub>2</sub>	2.5×10 <sup>-14</sup> 2.5×10 <sup>-14</sup>	±0.5 ±0.5	3.3×10 <sup>-12</sup> exp(-1450/ <i>T</i> ) 4.6×10 <sup>-12</sup> exp(-1560/ <i>T</i> )	280-370 280-370	±500 ±500
103	Cl+CH <sub>3</sub> CF <sub>2</sub> Cl → HCl+CH <sub>2</sub> CF <sub>2</sub> Cl	4.1×10 <sup>-16</sup>	±0.15	1.4×10 <sup>-12</sup> exp(-2420/ <i>T</i> )	296-440	±500
104	Cl+CH <sub>3</sub> CFCl <sub>2</sub> → HCl+CH <sub>2</sub> CFCl <sub>2</sub>	2.1×10 <sup>-15</sup>	±0.1	1.7×10 <sup>-12</sup> exp(-2000/ <i>T</i> )	290-380	±300

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105	$\text{Cl} + \text{CH}_3\text{CCl}_3 \rightarrow \text{HCl} + \text{CH}_2\text{CCl}_3$	$7 \times 10^{-15}$	$\pm 0.2$	$2.8 \times 10^{-12} \exp(-1790/T)$	290–420	$\pm 400$
106	$\text{Cl} + \text{CH}_2\text{FCF}_3 \rightarrow \text{HCl} + \text{CHF}_2\text{CF}_3$	$1.5 \times 10^{-15}$	$\pm 0.1$	$3.4 \times 10^{-12} \exp(-2300/T)$	299–430	$\pm 500$
107	$\text{Cl} + \text{CHF}_2\text{CHF}_2 \rightarrow \text{HCl} + \text{CF}_2\text{CHF}_2$	$2.2 \times 10^{-15}$	$\pm 0.2$	$7.9 \times 10^{-12} \exp(-2440/T)$	280–360	$\pm 500$
108	$\text{Cl} + \text{CHF}_2\text{CF}_3 \rightarrow \text{HCl} + \text{CF}_2\text{CF}_3$	$2.5 \times 10^{-16}$	$\pm 0.2$			
109	$\text{Cl} + \text{CHFClCF}_3 \rightarrow \text{HCl} + \text{CFClCF}_3$	$2.7 \times 10^{-15}$	$\pm 0.1$	$1.1 \times 10^{-12} \exp(-1800/T)$	270–380	$\pm 500$
110	$\text{Cl} + \text{CHCl}_2\text{CF}_3 \rightarrow \text{HCl} + \text{CCl}_2\text{CF}_3$	$1.2 \times 10^{-14}$	$\pm 0.1$	$4.4 \times 10^{-12} \exp(-1740/T)$	270–380	$\pm 500$
111	$\text{HO} + \text{CH}_3\text{Cl} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{Cl}$	$3.6 \times 10^{-14}$	$\pm 0.10$	$2.1 \times 10^{-12} \exp(-1210/T)$	220–300	$\pm 200$
112	$\text{HO} + \text{CH}_2\text{FCl} \rightarrow \text{H}_2\text{O} + \text{CHFCl}$	$3.9 \times 10^{-14}$	$\pm 0.1$	$1.6 \times 10^{-12} \exp(-1105/T)$	240–300	$\pm 200$
113	$\text{HO} + \text{CH}_2\text{Cl}_2 \rightarrow \text{H}_2\text{O} + \text{CHCl}_2$	$1.0 \times 10^{-13}$	$\pm 0.10$	$1.8 \times 10^{-12} \exp(-860/T)$	210–400	$\pm 150$
114	$\text{HO} + \text{CHF}_2\text{Cl} \rightarrow \text{H}_2\text{O} + \text{CF}_2\text{Cl}$	$4.7 \times 10^{-15}$	$\pm 0.08$	$7.9 \times 10^{-13} \exp(-1530/T)$	240–300	$\pm 150$
115	$\text{HO} + \text{CHFCl}_2 \rightarrow \text{H}_2\text{O} + \text{CFCl}_2$	$2.9 \times 10^{-14}$	$\pm 0.1$	$1.04 \times 10^{-12} \exp(-1065/T)$	240–300	$\pm 200$
116	$\text{HO} + \text{CHCl}_3 \rightarrow \text{H}_2\text{O} + \text{CCl}_3$	$1.05 \times 10^{-13}$	$\pm 0.10$	$1.8 \times 10^{-12} \exp(-850/T)$	240–300	$\pm 300$
117	$\text{HO} + \text{CF}_2\text{Cl}_2 \rightarrow \text{HOCl} + \text{CF}_2\text{Cl}$	$< 7 \times 10^{-18}$		$< 1 \times 10^{-12} \exp(-3540/T)$	250–480	
118	$\text{HO} + \text{CFCl}_3 \rightarrow \text{HOCl} + \text{CFCl}_2$	$< 5 \times 10^{-18}$		$< 1 \times 10^{-12} \exp(-3650/T)$	250–480	
119	$\text{HO} + \text{CCl}_4 \rightarrow \text{HOCl} + \text{CCl}_3$	$< 5 \times 10^{-16}$		$< 1 \times 10^{-12} \exp(-2260/T)$	250–300	
120	$\text{HO} + \text{C}_2\text{HCl}_3 \rightarrow \text{products}$	$2.0 \times 10^{-12}$	$\pm 0.10$	$3.0 \times 10^{-13} \exp(565/T)$	230–300	$\pm 200$
121	$\text{HO} + \text{C}_2\text{Cl}_4 \rightarrow \text{products}$	$1.6 \times 10^{-13}$	$\pm 0.10$	$3.5 \times 10^{-12} \exp(-920/T)$	290–420	$\pm 300$
122	$\text{HO} + \text{CH}_3\text{CF}_2\text{Cl} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CF}_2\text{Cl}$	$3.0 \times 10^{-15}$	$\pm 0.10$	$8.5 \times 10^{-13} \exp(-1685/T)$	220–300	$\pm 200$
123	$\text{HO} + \text{CH}_3\text{CFCl}_2 \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CFCl}_2$	$5.8 \times 10^{-15}$	$\pm 0.10$	$8.1 \times 10^{-13} \exp(-1470/T)$	220–300	$\pm 200$
124	$\text{HO} + \text{CH}_3\text{CCl}_3 \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CCl}_3$	$9.5 \times 10^{-15}$	$\pm 0.10$	$1.2 \times 10^{-12} \exp(-1440/T)$	240–300	$\pm 200$
125	$\text{HO} + \text{CH}_2\text{ClCF}_3 \rightarrow \text{H}_2\text{O} + \text{CHClCF}_3$	$1.4 \times 10^{-14}$	$\pm 0.15$	$5.6 \times 10^{-13} \exp(-1100/T)$	260–380	$\pm 200$
126	$\text{HO} + \text{CH}_2\text{ClCF}_2\text{Cl} \rightarrow \text{H}_2\text{O} + \text{CHClCF}_2\text{Cl}$	$1.7 \times 10^{-14}$	$\pm 0.15$	$3.5 \times 10^{-12} \exp(-1585/T)$	250–350	$\pm 300$
127	$\text{HO} + \text{CHFClCF}_3 \rightarrow \text{H}_2\text{O} + \text{CFClCF}_3$	$8.7 \times 10^{-15}$	$\pm 0.20$	$3.5 \times 10^{-13} \exp(-1105/T)$	210–300	$\pm 300$
128	$\text{HO} + \text{CHCl}_2\text{CF}_3 \rightarrow \text{H}_2\text{O} + \text{CCl}_2\text{CF}_3$	$3.6 \times 10^{-14}$	$\pm 0.10$	$6.6 \times 10^{-13} \exp(-870/T)$	210–300	$\pm 200$
129	$\text{HO} + \text{CHFClCF}_2\text{Cl} \rightarrow \text{H}_2\text{O} + \text{CFClCF}_2\text{Cl}$	$1.2 \times 10^{-14}$	$\pm 0.3$	$8.4 \times 10^{-13} \exp(-1255/T)$	290–460	$\pm 400$
130	$\text{HO} + \text{CHCl}_2\text{CF}_2\text{Cl} \rightarrow \text{H}_2\text{O} + \text{CCl}_2\text{CF}_2\text{Cl}$	$5.1 \times 10^{-14}$	$\pm 0.2$	$8.1 \times 10^{-13} \exp(-825/T)$	270–340	$\pm 200$

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131	$\text{HO} + \text{CHFClCFCl}_2 \rightarrow \text{H}_2\text{O} + \text{CFClCFCl}_2$	$1.6 \times 10^{-14}$	$\pm 0.3$	$5.8 \times 10^{-13} \exp(-1065/T)$	270–340	$\pm 400$
132	$\text{HO} + \text{CHCl}_2\text{CF}_2\text{CF}_3 \rightarrow \text{H}_2\text{O} + \text{CCl}_2\text{CF}_2\text{CF}_3$	$2.5 \times 10^{-14}$	$\pm 0.15$	$1.1 \times 10^{-12} \exp(-1130/T)$	270–400	$\pm 300$
133	$\text{HO} + \text{CHFClCF}_2\text{CF}_2\text{Cl} \rightarrow \text{H}_2\text{O} + \text{CFClCF}_2\text{CF}_2\text{Cl}$	$8.9 \times 10^{-15}$	$\pm 0.10$	$5.5 \times 10^{-13} \exp(-1230/T)$	290–400	$\pm 300$
134	$\text{HO} + \text{CH}_3\text{CF}_2\text{CFCl}_2 \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CF}_2\text{CFCl}_2$	$2.4 \times 10^{-15}$	$\pm 0.3$	$7.0 \times 10^{-13} \exp(-1690/T)$	290–370	$\pm 300$
135	$\text{HO} + \text{HC(O)Cl} \rightarrow \text{H}_2\text{O} + \text{ClCO}$	$< 5 \times 10^{-13}$				
136	$\text{HO} + \text{CH}_3\text{OCl} \rightarrow \text{products}$	$7.2 \times 10^{-13}$	$\pm 0.3$	$2.4 \times 10^{-12} \exp(-360/T)$	250–350	$\pm 300$
137	$\text{HO} + \text{COCl}_2 \rightarrow \text{products}$	$< 5 \times 10^{-15}$				
138	$\text{HO} + \text{CH}_2\text{ClCHO} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{ClCO}$ $\rightarrow \text{H}_2\text{O} + \text{CHClCHO}$					
	<b>overall</b>	$3.1 \times 10^{-12}$	$\pm 0.15$			
139	$\text{HO} + \text{CHFClCHO} \rightarrow \text{H}_2\text{O} + \text{CHFClCO}$ $\rightarrow \text{H}_2\text{O} + \text{CFClCHO}$					
	<b>overall</b>	$2.1 \times 10^{-12}$	$\pm 0.15$			
140	$\text{HO} + \text{CHCl}_2\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CHCl}_2\text{CO}$ $\rightarrow \text{H}_2\text{O} + \text{CCl}_2\text{CHO}$					
	<b>overall</b>	$2.4 \times 10^{-12}$	$\pm 0.15$			
141	$\text{HO} + \text{CF}_2\text{ClCHO} \rightarrow \text{H}_2\text{O} + \text{CF}_2\text{ClCO}$	$8.2 \times 10^{-13}$	$\pm 0.25$			
142	$\text{HO} + \text{CFCl}_2\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CFCl}_2\text{CO}$	$1.2 \times 10^{-12}$	$\pm 0.15$			
143	$\text{HO} + \text{CCl}_3\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CCl}_3\text{CO}$	$8.0 \times 10^{-13}$	$\pm 0.15$	$1.8 \times 10^{-12} \exp(-240/T)$	230–420	$\pm 200$
144	$\text{HO} + \text{CH}_3\text{COCl} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{COCl}$	$6.8 \times 10^{-14}$	$\pm 0.3$			
145	$\text{HO} + \text{CHF}_2\text{OCHClCF}_3 \rightarrow \text{H}_2\text{O} + \text{CHF}_2\text{OCClCF}_3$ $\rightarrow \text{H}_2\text{O} + \text{CF}_2\text{OCHClCF}_3$					
	<b>overall</b>	$1.5 \times 10^{-14}$	$\pm 0.10$	$1.1 \times 10^{-12} \exp(-1280/T)$	250–430	$\pm 250$
146	$\text{HO} + \text{CHF}_2\text{OCF}_2\text{CHCl} \rightarrow \text{H}_2\text{O} + \text{CHF}_2\text{OCF}_2\text{CHCl}$ $\rightarrow \text{H}_2\text{O} + \text{CF}_2\text{OCF}_2\text{CHCl}$					
	<b>overall</b>	$1.2 \times 10^{-14}$	$\pm 0.10$	$7.5 \times 10^{-13} \exp(-1230/T)$	250–430	$\pm 150$

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Reaction number	Reaction	$k_{298}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/\text{K}^a$
147	$\text{HO}_2 + \text{CF}_3\text{CCl}_2\text{O}_2 \rightarrow \text{O}_2 + \text{CF}_3\text{CCl}_2\text{O}_2\text{H}$	$1.9 \times 10^{-12}$	$\pm 0.3$			
148	$\text{HO}_2 + \text{CH}_2\text{ClO}_2 \rightarrow \text{CH}_2\text{ClO}_2\text{H} + \text{O}_2$ $\rightarrow \text{HC(O)Cl} + \text{H}_2\text{O} + \text{O}_2$					
	<b>overall</b>	$5.0 \times 10^{-12}$	$\pm 0.3$	$3.2 \times 10^{-13} \exp(820/T)$	250–600	$\pm 300$
149	$\text{HO}_2 + \text{CHCl}_2\text{O}_2 \rightarrow \text{CHCl}_2\text{O}_2\text{H} + \text{O}_2$ $\rightarrow \text{C(O)Cl}_2 + \text{H}_2\text{O} + \text{O}_2$ $\rightarrow \text{HC(O)Cl} + \text{HOCl} + \text{O}_2$	$4.1 \times 10^{-12}$ $1.8 \times 10^{-12}$				
	<b>overall</b>	$5.9 \times 10^{-12}$	$\pm 0.3$	$5.6 \times 10^{-13} \exp(700/T)$	280–440	$\pm 300$
150	$\text{HO}_2 + \text{CF}_2\text{ClO}_2 \rightarrow \text{O}_2 + \text{CF}_2\text{ClO}_2\text{H}$ $\rightarrow \text{O}_2 + \text{COF}_2 + \text{HOCl}$ $\rightarrow \text{O}_2 + \text{FCOCl} + \text{HOF}$					
	<b>overall</b>	$3.4 \times 10^{-12}$	$\pm 0.5$			
151	$\text{HO}_2 + \text{CCl}_3\text{O}_2 \rightarrow \text{CCl}_3\text{O}_2\text{H} + \text{O}_2$ $\rightarrow \text{C(O)Cl}_2 + \text{HOCl} + \text{O}_2$	$5.1 \times 10^{-12}$				
	<b>overall</b>	$5.1 \times 10^{-12}$	$\pm 0.3$	$4.7 \times 10^{-13} \exp(710/T)$	280–440	$\pm 300$
152	$\text{HO}_2 + \text{CFCl}_2\text{CH}_2\text{O}_2 \rightarrow \text{O}_2 + \text{CFCl}_2\text{CH}_2\text{O}_2\text{H}$ $\rightarrow \text{O}_2 + \text{CFCl}_2\text{CHO} + \text{H}_2\text{O}$					
	<b>overall</b>	$9.2 \times 10^{-12}$	$\pm 0.5$			
153	$\text{HO}_2 + \text{CF}_2\text{ClCH}_2\text{O}_2 \rightarrow \text{O}_2 + \text{CF}_2\text{ClCH}_2\text{O}_2\text{H}$ $\rightarrow \text{O}_2 + \text{CF}_2\text{ClCHO} + \text{H}_2\text{O}$					
	<b>overall</b>	$6.8 \times 10^{-12}$	$\pm 0.5$			
154	$\text{NO}_3 + \text{C}_2\text{HCl}_3 \rightarrow \text{products}$	$3.5 \times 10^{-16}$	$\pm 0.2$	$3.2 \times 10^{-13} \exp(-2030/T)$	270–370	$\pm 500$
155	$\text{NO}_3 + \text{C}_2\text{Cl}_4 \rightarrow \text{products}$	$< 1 \times 10^{-16}$				

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Reaction number	Reaction	$k_{298}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/\text{K}^a$
156	$\text{ClO} + \text{CH}_3\text{O}_2 \rightarrow \text{ClOO} + \text{CH}_3\text{O}$ $\rightarrow \text{OCIO} + \text{CH}_3\text{O}$ $\rightarrow \text{HCHO} + \text{HCl} + \text{O}_2$ $\rightarrow \text{CH}_3\text{Cl} + \text{O}_3$ $\rightarrow \text{CH}_3\text{OCl} + \text{O}_2$	$1.6 \times 10^{-12}$		See data sheet		
	<b>overall</b>	$3.3 \times 10^{-13}$ $2.2 \times 10^{-12}$		See data sheet $2.4 \times 10^{-12} \exp(-20/T)$	220–360	$\pm 200$
157	$\text{CF}_2\text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{CF}_2\text{ClO}_2 + \text{M}$	$1.4 \times 10^{-29} [\text{N}_2]$ $7 \times 10^{-12}$ $F_c = 0.4$	$(k_0) \pm 0.5$ $(k_\infty) \pm 0.5$	$1.4 \times 10^{-29} (T/300)^{-5} [\text{N}_2]$ $7 \times 10^{-12} (T/298)^{-0.6}$ $F_c = 0.4$	200–300 200–300	$\Delta n = \pm 3$ $\Delta n = \pm 0.5$
158	$\text{CFCl}_2 + \text{O}_2 + \text{M} \rightarrow \text{CFCl}_2\text{O}_2 + \text{M}$	$6 \times 10^{-30} [\text{N}_2]$ $9 \times 10^{-12}$ $F_c \approx 0.4$	$(k_0) \pm 0.3$ $(k_\infty) \pm 0.3$	$6 \times 10^{-30} (T/298)^{-6} [\text{N}_2]$ $9 \times 10^{-12}$ $F_c \approx 0.4$	230–380 230–300 230–380	$\Delta n = \pm 3$ $\Delta n = \pm 1$
159	$\text{CCl}_3 + \text{O}_2 + \text{M} \rightarrow \text{CCl}_3\text{O}_2 + \text{M}$	$1.1 \times 10^{-30} [\text{N}_2]$ $5.2 \times 10^{-12}$ $F_c = 0.35$	$(k_0) \pm 0.2$ $(k_\infty) \pm 0.3$	$1.1 \times 10^{-30} (T/300)^{-6.2} [\text{N}_2]$ $5.2 \times 10^{-12} (T/300)^{-1.4}$ $F_c = 0.35$	230–350 260–350 230–350	$\Delta n = \pm 1$ $\Delta n = \pm 1$
160	$\text{CHFClO} + \text{O}_2 \rightarrow \text{COFCl} + \text{HO}_2$			See data sheet		
161	$\text{CHFClO} + \text{M} \rightarrow \text{HCOF} + \text{Cl} + \text{M}$			See data sheet		
162	$\text{CF}_2\text{ClO} + \text{O}_2 \rightarrow \text{products}$			See data sheet		
163	$\text{CF}_2\text{ClO} + \text{M} \rightarrow \text{COF}_2 + \text{Cl} + \text{M}$			See data sheet		
164	$\text{CFCl}_2\text{O} + \text{O}_2 \rightarrow \text{products}$			See data sheet		
165	$\text{CFCl}_2\text{O} + \text{M} \rightarrow \text{COFCl} + \text{Cl} + \text{M}$			See data sheet		
166	$\text{CCl}_3\text{O} + \text{M} \rightarrow \text{COCl}_2 + \text{Cl}$			See data sheet		
167	$\text{CF}_2\text{ClCH}_2\text{O} + \text{O}_2 \rightarrow \text{CF}_2\text{ClCHO} + \text{HO}_2$			See data sheet		
168	$\text{CF}_2\text{ClCH}_2\text{O} + \text{M} \rightarrow \text{CF}_2\text{Cl} + \text{HCHO} + \text{M}$			See data sheet		
169	$\text{CFCl}_2\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CFCl}_2\text{CHO} + \text{HO}_2$			See data sheet		
170	$\text{CFCl}_2\text{CH}_2\text{O} + \text{M} \rightarrow \text{CFCl}_2 + \text{HCHO} + \text{M}$			See data sheet		

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171	$\text{CF}_3\text{CFClO} + \text{O}_2 \rightarrow \text{products}$			See data sheet		
172	$\text{CF}_3\text{CFClO} + \text{M} \rightarrow \text{CF}_3\text{COF} + \text{Cl} + \text{M}$			See data sheet		
173	$\text{CF}_3\text{CCl}_2\text{O} + \text{O}_2 \rightarrow \text{products}$			See data sheet		
174	$\text{CF}_3\text{CCl}_2\text{O} + \text{M} \rightarrow \text{CF}_3\text{COCl} + \text{Cl} + \text{M}$			See data sheet		
175	$\text{CF}_3\text{CF}_2\text{CCl}_2\text{O} + \text{O}_2 \rightarrow \text{products}$			See data sheet		
176	$\text{CF}_3\text{CF}_2\text{CCl}_2\text{O} + \text{M} \rightarrow \text{CF}_3\text{CF}_2\text{COCl} + \text{Cl} + \text{M}$			See data sheet		
177	$\text{CF}_2\text{ClCF}_2\text{CFClO} + \text{O}_2 \rightarrow \text{products}$			See data sheet		
178	$\text{CF}_2\text{ClCF}_2\text{CFClO} + \text{M} \rightarrow \text{CF}_2\text{ClCF}_2\text{COF} + \text{Cl} + \text{M}$			See data sheet		
179	$\text{CH}_2\text{ClO} + \text{O}_2 \rightarrow \text{HCOCl} + \text{HO}_2$			See data sheet		
180	$\text{CH}_2\text{ClO} + \text{M} \rightarrow \text{HCO} + \text{HCl} + \text{M}$			See data sheet		
181	$\text{CH}_3\text{CHClO} + \text{O}_2 \rightarrow \text{CH}_3\text{COCl} + \text{HO}_2$			See data sheet		
182	$\text{CH}_3\text{CHClO} + \text{M} \rightarrow \text{CH}_3\text{CO} + \text{HCl} + \text{M}$			See data sheet		
183	$\text{HOCH}_2\text{CHClO} + \text{O}_2 \rightarrow \text{HOCH}_2\text{COCl} + \text{HO}_2$			See data sheet		
184	$\text{HOCH}_2\text{CHClO} + \text{M} \rightarrow \text{CH}_2\text{OH} + \text{HCOCl} + \text{M}$			See data sheet		
185	$\text{HOCHClCH}_2\text{O} + \text{O}_2 \rightarrow \text{HOCHClCHO} + \text{HO}_2$			See data sheet		
186	$\text{HOCHClCH}_2\text{O} + \text{M} \rightarrow \text{CHClOH} + \text{HCHO} + \text{M}$			See data sheet		
187	$\text{CH}_3\text{CCl}_2\text{O} + \text{O}_2 \rightarrow \text{products}$			See data sheet		
188	$\text{CH}_3\text{CCl}_2\text{O} + \text{M} \rightarrow \text{CH}_3\text{COCl} + \text{Cl} + \text{M}$			See data sheet		
189	$\text{CCl}_3\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CCl}_3\text{CHO} + \text{HO}_2$			See data sheet		
190	$\text{CCl}_3\text{CH}_2\text{O} + \text{M} \rightarrow \text{CCl}_3 + \text{HCHO} + \text{M}$			See data sheet		
191	$\text{CCl}_3\text{CCl}_2\text{O} + \text{O}_2 \rightarrow \text{products}$			See data sheet		
192	$\text{CCl}_3\text{CCl}_2\text{O} + \text{M} \rightarrow \text{CCl}_3\text{COCl} + \text{Cl} + \text{M}$			See data sheet		
193	$\text{CH}_2\text{ClO}_2 + \text{NO} \rightarrow \text{CH}_2\text{ClO} + \text{NO}_2$	$1.9 \times 10^{-11}$	$\pm 0.3$			
194	$\text{CHFClO}_2 + \text{NO} \rightarrow \text{CHFClO} + \text{NO}_2$	$1.3 \times 10^{-11}$	$\pm 0.3$			

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195	CF <sub>2</sub> ClO <sub>2</sub> +NO → CF <sub>2</sub> ClO+NO <sub>2</sub>	1.5×10 <sup>-11</sup>	±0.2	1.5×10 <sup>-11</sup> (T/298) <sup>-1.5</sup>	230-430	Δ <i>n</i> =±0.5
196	CFCl <sub>2</sub> O <sub>2</sub> +NO → CFCl <sub>2</sub> O+NO <sub>2</sub>	1.5×10 <sup>-11</sup>	±0.2	1.5×10 <sup>-11</sup> (T/298) <sup>-1.3</sup>	230-430	Δ <i>n</i> =±0.5
197	CCl <sub>3</sub> O <sub>2</sub> +NO → CCl <sub>3</sub> O+NO <sub>2</sub>	1.8×10 <sup>-11</sup>	±0.2	1.8×10 <sup>-11</sup> (T/298) <sup>-1.0</sup>	230-430	Δ <i>n</i> =±0.5
198	CH <sub>3</sub> CFClO <sub>2</sub> +NO → CH <sub>3</sub> CFClO+NO <sub>2</sub>	2.0×10 <sup>-11</sup>	±0.3	2.0×10 <sup>-11</sup> (T/298) <sup>-1.8</sup>	260-320	Δ <i>n</i> =±0.5
199	CF <sub>2</sub> ClCH <sub>2</sub> O <sub>2</sub> +NO → CF <sub>2</sub> ClCH <sub>2</sub> O+NO <sub>2</sub>	1.2×10 <sup>-11</sup>	±0.3			
200	CFCl <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> +NO +M → CFCl <sub>2</sub> CH <sub>2</sub> O+NO <sub>2</sub>	1.3×10 <sup>-11</sup>	±0.2	1.3×10 <sup>-11</sup> (T/298) <sup>-1.5</sup>	260-320	Δ <i>n</i> =±0.5
201	CF <sub>3</sub> CCl <sub>2</sub> O <sub>2</sub> +NO → CF <sub>3</sub> CCl <sub>2</sub> O+NO <sub>2</sub>	1.8×10 <sup>-11</sup>	±0.3			
202	CH <sub>2</sub> ClCH <sub>2</sub> O <sub>2</sub> +NO → CH <sub>2</sub> ClCH <sub>2</sub> O+NO <sub>2</sub>	9.7×10 <sup>-12</sup>	±0.3			
203	CF <sub>2</sub> ClO <sub>2</sub> +NO <sub>2</sub> +M → CF <sub>2</sub> ClO <sub>2</sub> NO <sub>2</sub> + M	5.0×10 <sup>-29</sup> [N <sub>2</sub> ] 6.3×10 <sup>-12</sup> <i>F<sub>c</sub></i> =0.30	( <i>k<sub>0</sub></i> ) ±0.3 ( <i>k<sub>∞</sub></i> ) ±0.3	5.0×10 <sup>-29</sup> (T/298) <sup>-6.2</sup> [N <sub>2</sub> ] 6.3×10 <sup>-12</sup> (T/298) <sup>-0.7</sup> <i>F<sub>c</sub></i> =0.30	250–320 250–320 250–320	Δ <i>n</i> =±2 Δ <i>n</i> =±0.5
204	CF <sub>2</sub> ClO <sub>2</sub> NO <sub>2</sub> +M → CF <sub>2</sub> ClO <sub>2</sub> +NO <sub>2</sub> + M	9.0×10 <sup>-19</sup> [N <sub>2</sub> ] 5.4×10 <sup>-2</sup> <i>F<sub>c</sub></i> =0.30	( <i>k<sub>0</sub></i> /s <sup>-1</sup> ) ±0.3 ( <i>k<sub>∞</sub></i> /s <sup>-1</sup> ) ±0.3	1.8×10 <sup>-3</sup> exp(-10 500/T) [N <sub>2</sub> ] 1.6×10 <sup>16</sup> exp(-11 990/T) <i>F<sub>c</sub></i> =0.30	270–290 270–290 270–290	±200 ±200
205	CFCl <sub>2</sub> O <sub>2</sub> +NO <sub>2</sub> +M → CFCl <sub>2</sub> O <sub>2</sub> NO <sub>2</sub> + M	5.5×10 <sup>-29</sup> [N <sub>2</sub> ] 8.3×10 <sup>-12</sup> <i>F<sub>c</sub></i> =0.42	( <i>k<sub>0</sub></i> ) ±0.3 ( <i>k<sub>∞</sub></i> ) ±0.2	5.5×10 <sup>-29</sup> (T/298) <sup>-5.5</sup> [N <sub>2</sub> ] 8.3×10 <sup>-12</sup> (T/298) <sup>-0.66</sup> <i>F<sub>c</sub></i> =0.42	230–380 230–380 230–380	Δ <i>n</i> =±2 Δ <i>n</i> =±0.5
206	CFCl <sub>2</sub> O <sub>2</sub> NO <sub>2</sub> +M → CFCl <sub>2</sub> O <sub>2</sub> +NO <sub>2</sub> + M	1.5×10 <sup>-18</sup> [N <sub>2</sub> ] 9.6×10 <sup>-2</sup> <i>F<sub>c</sub></i> =0.28	( <i>k<sub>0</sub></i> /s <sup>-1</sup> ) ±0.3 ( <i>k<sub>∞</sub></i> /s <sup>-1</sup> ) ±0.3	1.0×10 <sup>-2</sup> exp(-10 860/T) [N <sub>2</sub> ] 6.6×10 <sup>16</sup> exp(-12 240/T) <i>F<sub>c</sub></i> =0.28	260–300 260–300 260–300	±200 ±500
207	CCl <sub>3</sub> O <sub>2</sub> +NO <sub>2</sub> +M → CCl <sub>3</sub> O <sub>2</sub> NO <sub>2</sub> +M	9.2×10 <sup>-29</sup> [N <sub>2</sub> ] 1.5×10 <sup>-12</sup> <i>F<sub>c</sub></i> =0.32	( <i>k<sub>0</sub></i> ) ±0.3 ( <i>k<sub>∞</sub></i> ) ±0.3	9.2×10 <sup>-29</sup> (T/298) <sup>-6.0</sup> [N <sub>2</sub> ] 1.5×10 <sup>-12</sup> (T/298) <sup>-0.7</sup> <i>F<sub>c</sub></i> =0.32	230–380 230–380 230–380	Δ <i>n</i> =±2 Δ <i>n</i> =±0.5
208	CCl <sub>3</sub> O <sub>2</sub> NO <sub>2</sub> +M → CCl <sub>3</sub> O <sub>2</sub> +NO <sub>2</sub> +M	5.2×10 <sup>-18</sup> [N <sub>2</sub> ] 0.29 <i>F<sub>c</sub></i> =0.32	( <i>k<sub>0</sub></i> /s <sup>-1</sup> ) ±0.3 ( <i>k<sub>∞</sub></i> /s <sup>-1</sup> ) ±0.3	4.3×10 <sup>-3</sup> exp(-10 235/T) [N <sub>2</sub> ] 4.8×10 <sup>16</sup> exp(-11 820/T) <i>F<sub>c</sub></i> =0.32	260–300 260–300 260–300	±500 ±500

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Reaction number	Reaction	$k_{298}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$\Delta \log k_{298}^a$	Temp. dependence of $k$ /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp. range/K	$\Delta(E/R)/K^a$
209	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> +CF <sub>3</sub> CCl <sub>2</sub> O <sub>2</sub> → CH <sub>3</sub> CHO+CF <sub>3</sub> CCl <sub>2</sub> OH+O <sub>2</sub> → C <sub>2</sub> H <sub>5</sub> O+CF <sub>3</sub> CCl <sub>2</sub> O+O <sub>2</sub>	3.6×10 <sup>-12</sup> 9×10 <sup>-13</sup>	±0.3 ±0.5			
210	CF <sub>2</sub> ClCH <sub>2</sub> O <sub>2</sub> +CF <sub>2</sub> ClCH <sub>2</sub> O <sub>2</sub> → CF <sub>2</sub> ClCH <sub>2</sub> OH+CF <sub>2</sub> ClCHO+O <sub>2</sub> → CF <sub>2</sub> ClCH <sub>2</sub> O+CF <sub>2</sub> ClCH <sub>2</sub> O+O <sub>2</sub>	2.8×10 <sup>-12</sup>				
	<b>overall</b>	2.8×10 <sup>-12</sup>	±0.4			
211	CFCl <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> +CFCl <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> → CFCl <sub>2</sub> CH <sub>2</sub> OH+CFCl <sub>2</sub> CHO+O <sub>2</sub> → 2CFCl <sub>2</sub> CH <sub>2</sub> O+O <sub>2</sub>	2.9×10 <sup>-12</sup>				
	<b>overall</b>	2.9×10 <sup>-12</sup>	±0.4			
212	CF <sub>3</sub> CCl <sub>2</sub> O <sub>2</sub> +CF <sub>3</sub> CCl <sub>2</sub> O <sub>2</sub> → 2CF <sub>3</sub> CCl <sub>2</sub> O+O <sub>2</sub>	3.5 × 10 <sup>-12</sup>	±0.3			
213	CH <sub>2</sub> ClO <sub>2</sub> +CH <sub>2</sub> ClO <sub>2</sub> → CH <sub>2</sub> ClOH+HC(O)Cl+O <sub>2</sub> → 2CH <sub>2</sub> CClO+O <sub>2</sub>	3.5×10 <sup>-12</sup>				
	<b>overall</b>	3.5×10 <sup>-12</sup>	±0.2	1.9×10 <sup>-13</sup> exp(870/T)	250–600	±200
214	CHCl <sub>2</sub> O <sub>2</sub> +CHCl <sub>2</sub> O <sub>2</sub> → CH <sub>2</sub> Cl <sub>2</sub> OH+C(O)Cl <sub>2</sub> +O <sub>2</sub> → CHCl <sub>2</sub> O+CHCl <sub>2</sub> O+O <sub>2</sub>	See data sheet				
215	CCl <sub>3</sub> O <sub>2</sub> +CCl <sub>3</sub> O <sub>2</sub> → 2CCl <sub>3</sub> O+O <sub>2</sub>	4.0×10 <sup>-12</sup>	±0.3	3.3×10 <sup>-13</sup> exp(740/T)	270–460	±300
216	CH <sub>3</sub> CHClO <sub>2</sub> +CH <sub>3</sub> CHClO <sub>2</sub> → CH <sub>3</sub> CHClOH+CH <sub>3</sub> COCl+O <sub>2</sub> → 2CH <sub>3</sub> CHClO+O <sub>2</sub>	5×10 <sup>-12</sup>	±0.3			
	<b>overall</b>	See data sheet				

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217	$\text{CH}_2\text{ClCH}_2\text{O}_2 + \text{CH}_2\text{ClCH}_2\text{O}_2$ → $\text{CH}_2\text{ClCH}_2\text{OH} + \text{CH}_2\text{ClCHO} + \text{O}_2$ → $2\text{CH}_2\text{ClCH}_2\text{O} + \text{O}_2$ <b>overall</b>	$1.2 \times 10^{-12}$ $2.1 \times 10^{-12}$ $3.3 \times 10^{-12}$	$\pm 0.3$	$4.2 \times 10^{-14} \exp(1300/T)$	220–380	$\pm 500$
218	$\text{O}_3 + \text{C}_2\text{HCl}_3 \rightarrow \text{products}$	$< 5 \times 10^{-20}$				
219	$\text{O}_3 + \text{C}_2\text{Cl}_4 \rightarrow \text{products}$	$< 10^{-21}$				

*Data for the following Photochemical Reactions is based on data sheets on the IUPAC website updated in 2005*

220	$\text{CH}_3\text{Cl} + \text{h}\nu \rightarrow \text{products}$
221	$\text{CH}_3\text{OCl} + \text{h}\nu \rightarrow \text{products}$
222	$\text{CHF}_2\text{Cl} + \text{h}\nu \rightarrow \text{products}$
223	$\text{CF}_2\text{Cl}_2 + \text{h}\nu \rightarrow \text{products}$
224	$\text{CFCl}_3 + \text{h}\nu \rightarrow \text{products}$
225	$\text{CCl}_4 + \text{h}\nu \rightarrow \text{products}$
226	$\text{CH}_3\text{CF}_2\text{Cl} + \text{h}\nu \rightarrow \text{products}$
227	$\text{CH}_3\text{CFCl}_2 + \text{h}\nu \rightarrow \text{products}$
228	$\text{CH}_3\text{CCl}_3 + \text{h}\nu \rightarrow \text{products}$
229	$\text{CF}_3\text{CHFCl} + \text{h}\nu \rightarrow \text{products}$
230	$\text{CF}_3\text{CHCl}_2 + \text{h}\nu \rightarrow \text{products}$
231	$\text{CF}_2\text{ClCFCl}_2 + \text{h}\nu \rightarrow \text{products}$
232	$\text{CF}_2\text{ClCF}_2\text{Cl} + \text{h}\nu \rightarrow \text{products}$
233	$\text{CF}_3\text{CF}_2\text{Cl} + \text{h}\nu \rightarrow \text{products}$
234	$\text{CF}_3\text{CF}_2\text{CHCl}_2 + \text{h}\nu \rightarrow \text{products}$
235	$\text{CF}_2\text{ClCF}_2\text{CHFCl} + \text{h}\nu \rightarrow \text{products}$
236	$\text{HCOCl} + \text{h}\nu \rightarrow \text{products}$
237	$\text{COFCl} + \text{h}\nu \rightarrow \text{products}$

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Reaction number	Reaction	$k_{298}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/\text{K}^2$
238	$\text{COCl}_2 + h\nu \rightarrow \text{products}$					
239	$\text{CF}_2\text{ClCHO} + h\nu \rightarrow \text{products}$					
240	$\text{CFCl}_2\text{CHO} + h\nu \rightarrow \text{products}$					
241	$\text{CCl}_3\text{CHO} + h\nu \rightarrow \text{products}$					
242	$\text{CF}_3\text{COCl} + h\nu \rightarrow \text{products}$					
<b><math>\text{BrO}_x</math> Reactions - based on data sheets in Appendix 3, and on the IUPAC website updated in 2005</b>						
243	$\text{HO} + \text{CH}_3\text{Br} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{Br}$	$2.9 \times 10^{-14}$	$\pm 0.08$	$1.7 \times 10^{-12} \exp(-1215/T)$	240–300	$\pm 150$
244	$\text{HO} + \text{CH}_2\text{Br}_2 \rightarrow \text{H}_2\text{O} + \text{CHBr}_2$	$1.1 \times 10^{-13}$	$\pm 0.15$	$1.5 \times 10^{-12} \exp(-775/T)$	240–300	$\pm 200$
245	$\text{HO} + \text{CHF}_2\text{Br} \rightarrow \text{H}_2\text{O} + \text{CF}_2\text{Br}$	$1.0 \times 10^{-14}$	$\pm 0.10$	$7.9 \times 10^{-13} \exp(-1300/T)$	230–360	$\pm 150$
246	$\text{HO} + \text{CF}_3\text{Br} \rightarrow \text{products}$	$< 6.0 \times 10^{-18}$		$< 1 \times 10^{-12} \exp(-3600/T)$	250–460	
247	$\text{HO} + \text{CF}_2\text{ClBr} \rightarrow \text{products}$	$< 1 \times 10^{-17}$		$< 1 \times 10^{-12} \exp(-3450/T)$	250–380	
248	$\text{HO} + \text{CF}_2\text{Br}_2 \rightarrow \text{products}$	$< 5.0 \times 10^{-16}$		$< 1 \times 10^{-12} \exp(-2200/T)$	250–460	
249	$\text{HO} + \text{CF}_3\text{CH}_2\text{Br} \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CHBr}$	$1.6 \times 10^{-14}$	$\pm 0.2$	$1.4 \times 10^{-12} \exp(-1340/T)$	280–460	$\pm 300$
250	$\text{HO} + \text{CF}_3\text{CHFBr} \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CFBr}$	$1.7 \times 10^{-14}$	$\pm 0.2$	$8.1 \times 10^{-13} \exp(-1155/T)$	270–460	$\pm 300$
251	$\text{HO} + \text{CF}_3\text{CHClBr} \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CClBr}$	$4.6 \times 10^{-14}$	$\pm 0.20$	$1.2 \times 10^{-12} \exp(-970/T)$	290–460	$\pm 300$
252	$\text{HO} + \text{CF}_2\text{BrCF}_2\text{Br} \rightarrow \text{products}$	$< 6 \times 10^{-18}$		$< 1 \times 10^{-12} \exp(-3600/T)$	250–460	
253	$\text{HO}_2 + \text{CH}_2\text{BrO}_2 \rightarrow \text{O}_2 + \text{CH}_2\text{BrO}_2\text{H}$ $\rightarrow \text{O}_2 + \text{HC(O)Br} + \text{H}_2\text{O}$	$6.7 \times 10^{-12}$				
254	$\text{CH}_2\text{BrO}_2 + \text{NO} \rightarrow \text{CH}_2\text{BrO} + \text{NO}_2$	$1.1 \times 10^{-11}$	$\pm 0.3$			
255	$\text{CHBr}_2\text{O}_2 + \text{NO} \rightarrow \text{CHBr}_2\text{O} + \text{NO}_2$	$1.7 \times 10^{-11}$	$\pm 0.3$			
256	$\text{CH}_2\text{BrO}_2 + \text{CH}_2\text{BrO}_2$ $\rightarrow \text{HC(O)Br} + \text{CH}_2\text{BrOH} + \text{O}_2$ $\rightarrow 2\text{CH}_2\text{BrO} + \text{O}_2$	see data sheet				

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Reaction number	Reaction	$k_{298}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/\text{K}^a$
257	$\text{BrCH}_2\text{CH}_2\text{O}_2 + \text{BrCH}_2\text{CH}_2\text{O}_2$					
	$\rightarrow \text{BrCH}_2\text{CH}_2\text{OH} + \text{BrCH}_2\text{CHO} + \text{O}_2$	$1.7 \times 10^{-12}$				
	$\rightarrow 2\text{BrCH}_2\text{CH}_2\text{O} + \text{O}_2$	$2.3 \times 10^{-12}$				
	<b>overall</b>	$4.0 \times 10^{-12}$	$\pm 0.2$	$6.0 \times 10^{-14} \exp(1250/T)$	270-380	$\pm 500$
258	$\text{BrO} + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{BrOO}$	$1.4 \times 10^{-12}$				
	$\rightarrow \text{HOBr} + \text{CH}_2\text{O}_2$	$4.3 \times 10^{-12}$				
	<b>overall</b>	$5.7 \times 10^{-12}$	$\pm 0.3$			

Data for the following Photochemical Reactions is based on data sheets on the IUPAC website updated in 2006

259	$\text{CH}_3\text{Br} + h\nu \rightarrow \text{products}$
260	$\text{CF}_3\text{Br} + h\nu \rightarrow \text{products}$
261	$\text{CF}_2\text{ClBr} + h\nu \rightarrow \text{products}$
262	$\text{CF}_2\text{Br}_2 + h\nu \rightarrow \text{products}$
263	$\text{CHBr}_3 + h\nu \rightarrow \text{products}$
264	$\text{CF}_2\text{BrCF}_2\text{Br} + h\nu \rightarrow \text{products}$
265	$\text{CH}_2\text{Br}_2 + h\nu \rightarrow \text{products}$

$\text{IO}_x$  Reactions - based on data data sheets in Appendix 4, and on the IUPAC website updated in 2005

266	$\text{HO} + \text{CH}_3\text{I} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{I}$	$1.0 \times 10^{-13}$	$\pm 0.2$	$4.3 \times 10^{-12} \exp(-1120/T)$	270-430	$\pm 500$
267	$\text{HO} + \text{CF}_3\text{I} \rightarrow \text{products}$	$2.6 \times 10^{-14}$	$\pm 0.2$	$2.1 \times 10^{-11} \exp(-2000/T)$	270-370	$\pm 500$
268	$\text{CH}_2\text{IO}_2 + \text{CH}_2\text{IO}_2 \rightarrow \text{CH}_2\text{IOH} + \text{HC(O)I} + \text{O}_2$ $\rightarrow 2\text{CH}_2\text{IO} + \text{O}_2$	no recommendation				

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Reaction number	Reaction	$k_{298}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/\text{K}^2$
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*Data for the following Photochemical Reactions is based on data sheets on the IUPAC website updated in 2006*

269	$\text{CH}_3\text{I} + h\nu \rightarrow \text{products}$
270	$\text{CF}_3\text{I} + h\nu \rightarrow \text{products}$
271	$\text{CH}_2\text{ClI} + h\nu \rightarrow \text{products}$
272	$\text{CH}_2\text{BrI} + h\nu \rightarrow \text{products}$
273	$\text{CH}_2\text{I}_2 + h\nu \rightarrow \text{products}$

## 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.

### 5 1.1 Thermal reactions

The data sheets begin with a statement of the reactions including all pathways which are considered feasible. This is followed by the corresponding enthalpy changes at 298 K, calculated from the enthalpies of formation summarized in the Thermodynamics Data Summary, which is provided on the IUPAC website.

10 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 de-

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pendence 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:

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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

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TDLs – tunable diode laser spectroscopy  
UV – ultraviolet  
UVA – ultraviolet absorption  
VUVA – vacuum ultraviolet absorption

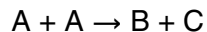
For measurements of relative rate coefficients, wherever possible the comments contain the actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient 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.

## 1.2 Conventions concerning rate coefficients

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



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

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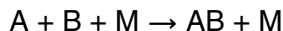
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Note that the stoichiometric coefficient for A, i.e. 2, appears in the denominator before the rate of change of [A] (which is equal to  $2k[A]^2$ ) and as a power on the righthand side.

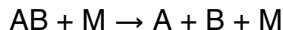
Representations of  $k$  as a function of temperature characterize simple “direct” bimolecular reactions. Sometimes it is found that  $k$  also depends on the pressure and the nature of the bath gas. This may be an indication of complex formation during the course of the bimolecular reaction, which is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

### 1.3 Treatment of combination and dissociation reactions

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



and the reverse dissociation reactions



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

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

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

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

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

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



while the dissociation reactions are characterized by:



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:

$$15 \quad k = k_1 \left( \frac{k_2[M]}{k_{-1} + k_2[M]} \right)$$

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.

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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

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

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

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):

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

The broadening factor  $F$  depends on the ratio  $k_0/k_\infty$ , which is proportional to  $[M]$ , and can be used as a measure of “reduced pressure”. The first factors on the right-hand

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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  $k_0$ ,  $k_\infty$ , 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  $k_\infty$ . In this case, the apparent values for  $F_c$ ,  $k_0$ , and  $k_\infty$  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  $k_\infty$  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  $k_\infty$  values. For the purpose of this evaluation, this is irrelevant if the preferred  $k_0$  and  $k_\infty$  are used consistently together with the preferred  $F_c$  values.

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If the selected  $F_c$  value is too large, the values of  $k_0$  and  $k_\infty$  obtained by fitting the falloff expression to the experimental data are underestimated. If  $F_c$  is too small,  $k_0$  and  $k_\infty$  are overestimated. However uncertainties in  $F_c$  influence the fitted  $k_0$  and  $k_\infty$  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  $k_\infty$  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  $k_\infty$  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  $k_\infty$ , provided  $F_c$  does not differ too much from the values given above. If large deviations are encountered, the experimental data are re-evaluated using the given  $F_c$ -values given above.

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



which, in the low pressure range, leads to

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

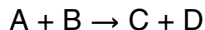
For some tri- and tetra-atomic adducts AB, e.g.  $O+O_2 \rightarrow O_3$  and  $Cl+O_2 \rightarrow ClOO$ , this value of  $k_0$  may exceed that from the energy-transfer mechanism and show stronger temperature as dependencies (Luther et al., 2005). This mechanism may also influence high pressure experiments when  $k_0$  from the radical-complex mechanism exceeds  $k_\infty$  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.

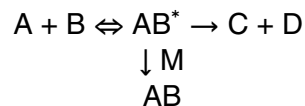
The dependence of  $k_0$  and  $k_\infty$  on the temperature  $T$  is represented in the form  $k \propto T^{-n}$  except for cases with an established energy barrier in the potential. We have used this form of temperature dependence because it usually gives a better fit to the data over a wider range 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  $k_\infty$ . In this evaluation, values of  $k_0$  are given for selected examples of third bodies M, and if possible for M=N<sub>2</sub>, O<sub>2</sub> or air.

#### 1.4 Treatment of complex-forming bimolecular reactions

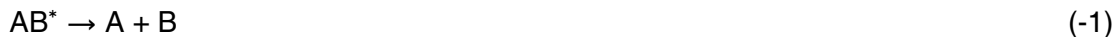
Bimolecular reactions may follow the “direct” pathway



and/or involve complex formation,



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



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

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

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

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

where

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

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

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

$$k_D \rightarrow K_1 k_3 / k_2$$

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

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

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where  $k_{D0}$  and  $k_{S0}$  are the respective limiting low-pressure rate coefficients for the formation of C+D or A+B at the considered [M]. When it is established that complex-formation is involved, this equation is used to characterize the increasing suppression of C+D formation with increasing [M]. One should also note that bimolecular reactions may have contributions from direct as well as complex-forming pathways leading to identical or different products.

## 1.5 Photochemical reactions

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

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

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

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

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## 1.6 Conventions concerning absorption cross sections

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

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

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

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

## 1.7 Assignment of uncertainties

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

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

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

5 The assignment of these absolute uncertainties in  $k$  and  $E/R$  is a subjective assessment of the evaluators. They are not determined by a rigorous, statistical analysis of the database, which is generally too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the techniques, the difficulties of the experimental measurements, the potential for systematic errors, and the number of studies  
10 conducted and their agreement or lack thereof. Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurement, i.e. the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 90% confidence limits, of  $\pm 10\%$  or less are frequently reported in the literature. Unfortunately,  
15 when evaluators compare data for the same reaction studied by more than one group of investigators and involving different techniques, the rate coefficients often differ by a factor of 2 or even more. This can only mean that one or more of the studies has involved large systematic uncertainty which is difficult to detect. This is hardly surprising since, unlike molecular reactions, it is not always possible to study atomic and  
20 free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise.

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  
25 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

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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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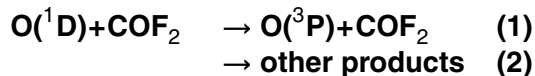
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Appendix 1: FO<sub>x</sub> Reactions

IV.A1.1



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

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

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

Comments

10 (a) Branching ratio was determined from the ratio of the O(<sup>3</sup>P) yield from O(<sup>1</sup>D)+COF<sub>2</sub> relative to that for O(<sup>1</sup>D)+N<sub>2</sub>.

Preferred Values

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

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## Reliability

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

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

## Comments on Preferred Values

- 5 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  $\text{COF}_2$  which might be important in the stratosphere is the reaction  $\text{O}(^1\text{D}) + \text{COF}_2 \rightarrow \text{F}_2 + \text{CO}_2$  and that this reaction would have to proceed by a complex mechanism involving an intermediate adduct.

## 10 References

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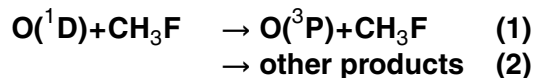
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## IV.A1.2



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

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.38 \pm 0.06) \times 10^{-10}$	298	Force and Wiesenfeld, 1981	PLP-RA
$(1.65 \pm 0.15) \times 10^{-10}$	298	Schmoltner et al., 1993	PLP-RF
<i>Branching Ratios</i>			
$k_1/k = 0.25 \pm 0.03$	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)  $\text{O}(^1\text{D})$  atoms were monitored by resonance absorption at 130.4 nm and compared to  $\text{O}(^3\text{P})$  atoms in the presence of ozone in He diluent where the  $\text{O}(^3\text{P})$  atom yield from the  $\text{O}(^1\text{D}) + \text{O}_3$  reaction is 1.0.
- (b) Branching ratio was determined from the ratio of the  $\text{O}(^3\text{P})$  yield from  $\text{O}(^1\text{D}) + \text{CH}_3\text{F}$  relative to that for  $\text{O}(^1\text{D}) + \text{N}_2$ .

## Preferred Values

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

$k_1/k = 0.18$  at 298 K.

## Reliability

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

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

## Comments on Preferred Values

10 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  $\text{O}(^3\text{P})$  was monitored and therefore no direct information relating to the products of the chemical reaction of  $\text{O}(^1\text{D}) + \text{CH}_3\text{F}$  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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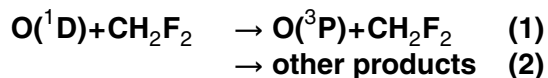
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### IV.A1.3



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

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

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

#### Comments

(a) Branching ratio was determined from the ratio of the  $\text{O}(^3\text{P})$  yield from  $\text{O}(^1\text{D}) + \text{CH}_2\text{F}_2$  relative to that for  $\text{O}(^1\text{D}) + \text{N}_2$ .

#### Preferred Values

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

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## Reliability

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

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

## Comments on Preferred Values

- 5 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  $O(^3P)$  was monitored and therefore no direct information relating to the products of the chemical reaction of  $O(^1D) + CH_2F_2$  was obtained. Burks and Lin (1981) have observed the appearance of stimulated emissions from vibrationally excited HF.

## 10 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.

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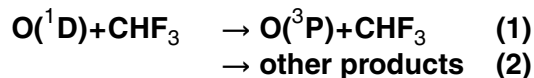
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#### IV.A1.4



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

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.4 \pm 0.8) \times 10^{-12}$	298	Force and Wiesenfeld, 1981	PLP-RA
$(9.76 \pm 0.60) \times 10^{-12}$	298	Schmoltner et al., 1993	PLP-RF
<i>Branching Ratios</i>			
$k_1/k = 0.77 \pm 0.15$	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)  $\text{O}(^1\text{D})$  atoms were monitored by resonance absorption at 130.4 nm and compared to  $\text{O}(^3\text{P})$  atoms in the presence of ozone in He diluent where the  $\text{O}(^3\text{P})$  atom yield from the  $\text{O}(^1\text{D})+\text{O}_3$  reaction is 1.0.

(b) Branching ratio was determined from the ratio of the  $\text{O}(^3\text{P})$  yield from  $\text{O}(^1\text{D})+\text{CHF}_3$  relative to that for  $\text{O}(^1\text{D})+\text{N}_2$ .

## Preferred Values

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

$k_1/k=0.9$  at 298 K.

## Reliability

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

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

## Comments on Preferred Values

10 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  $\text{O}(^3\text{P})$  was monitored and therefore no direct information relating to the products of the chemical reaction of  $\text{O}(^1\text{D}) + \text{CHF}_3$  was obtained. Burks and Lin (1981) and Aker et al. (1987) have observed the appearance of  
15 stimulated emissions from vibrationally excited HF.

## References

Aker, P. M., Niefer, B. I., Sloan, J. J., and Heydtmann, H.: J. Chem. Phys., 87, 203, 1987.

Burks, T. L. and Lin, M. C.: Int. J. Chem. Kinet., 13, 977, 1981.

20 Force, A. P., and Wiesenfeld, J. R.: J. Phys. Chem., 85, 782, 1981.

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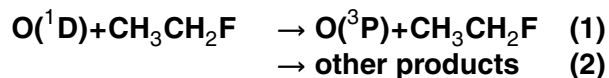
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## IV.A1.5



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

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

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

### Comments

(a) Branching ratio was determined from the ratio of the  $\text{O}(^3\text{P})$  yield from  $\text{O}(^1\text{D}) + \text{CH}_3\text{CH}_2\text{F}$  relative to that for  $\text{O}(^1\text{D}) + \text{N}_2$ .

### Preferred Values

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

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## Reliability

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

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

## Comments on Preferred Values

- 5 The preferred value of  $k$  and the preferred value of the branching ratio  $k_1/k$  are based on the results of Schmoltnner 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

- 10 Schmoltnner, 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.

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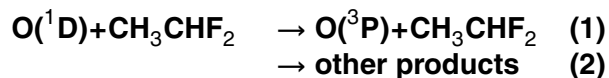
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## IV.A1.6



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

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

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

### Comments

(a) Branching ratio was determined from the ratio of the  $\text{O}(^3\text{P})$  yield from  $\text{O}(^1\text{D}) + \text{CH}_3\text{CHF}_2$  relative to that for  $\text{O}(^1\text{D}) + \text{N}_2$ .

### Preferred Values

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

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## Reliability

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

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

## Comments on Preferred Values

- 5 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(<sup>3</sup>P) was monitored and therefore no direct information relating to the products of the chemical reaction of O(<sup>1</sup>D)+CH<sub>3</sub>CHF<sub>2</sub> was obtained.

## References

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

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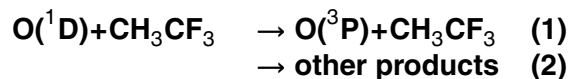
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## IV.A1.7



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

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<sup>5</sup> <i>Relative Rate Coefficients</i>			
$k_2 = (5.8 \pm 2.0) \times 10^{-11}$	297	Green and Wayne, 1976	RR (a)

### Comments

(a)  $\text{O}(^1\text{D})$  produced by photolysis of  $\text{NO}_2$  at 229 nm.  $\Delta(\text{CH}_3\text{CF}_3)/\Delta(\text{N}_2\text{O})$  monitored by IR absorption spectroscopy. Measured rate coefficient ratio of  $k_2/k(\text{O}(^1\text{D}) + \text{N}_2\text{O}) = 0.5 \pm 0.1$  is placed on an absolute basis by use of  $k(\text{O}(^1\text{D}) + \text{N}_2\text{O}) = 1.16 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current evaluation). The cited rate coefficient refers to chemical reaction only and does not include physical quenching.

### Preferred Values

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

## Reliability

$\Delta \log k = \pm 0.5$

## Comments on Preferred Values

5 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  $O(^1D)$ .

## References

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

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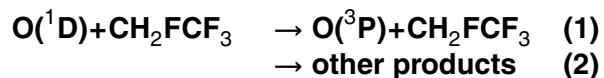
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#### IV.A1.8



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

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

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

#### Comments

(a) Branching ratio was determined from the ratio of the  $\text{O}(^3\text{P})$  yield from  $\text{O}(^1\text{D}) + \text{CH}_2\text{FCF}_3$  relative to that for  $\text{O}(^1\text{D}) + \text{N}_2$ .

#### Preferred Values

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

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## Reliability

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

$\Delta (k_1/k) = \begin{pmatrix} +0.06 \\ -0.10 \end{pmatrix}$

## Comments on Preferred Values

- 5 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

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

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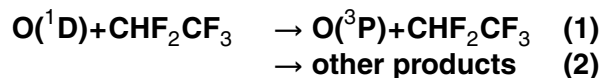
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## IV.A1.9



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

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

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

### Comments

(a) Branching ratio was determined from the ratio of the  $\text{O}(^3\text{P})$  yield from  $\text{O}(^1\text{D}) + \text{CHF}_2\text{CF}_3$  relative to that for  $\text{O}(^1\text{D}) + \text{N}_2$ .

### Preferred Values

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

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## Reliability

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

$\Delta (k_1/k) = \begin{pmatrix} +0.15 \\ -0.3 \end{pmatrix}$  at 298 K.

## 5 *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(<sup>3</sup>P) was monitored and therefore no direct information relating to the products of the chemical reaction of O(<sup>1</sup>D)+CHF<sub>2</sub>CF<sub>3</sub> was obtained.

## 10 **References**

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

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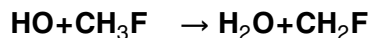
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## IV.A1.10



$$\Delta H^\circ = -78.2 \text{ kJ mol}^{-1}$$

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.60 \pm 0.35) \times 10^{-14}$	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	Schmoltnner et al., 1993	PLP/FP-LIF
<sup>5</sup> $(2.09 \pm 0.08) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$(1.71 \pm 0.08) \times 10^{-14}$	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)
$1.96 \times 10^{-14}$	298		
$4.21 \times 10^{-18} T^2 \exp[-(856 \pm 82)/T]$	308–393	DeMore, 1996	RR (f)

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## 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  $\text{CH}_3\text{ONO}$  at 933 mbar total pressure of air. The decay of  $\text{CH}_3\text{F}$  was inferred from the measured formation of  $\text{HC(O)F}$ , using a formation yield of  $\text{HC(O)F}$  of 0.90 as measured in separate  $\text{Cl}_2\text{-CH}_3\text{F-NO-air}$  irradiations. The concentrations of  $\text{HC(O)F}$  and acetylene were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CH}_3\text{F})/k(\text{HO}+\text{C}_2\text{H}_2)=0.0201\pm 0.0009$  was placed on an absolute basis by using  $k(\text{HO}+\text{C}_2\text{H}_2)=8.49\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 296 K and 1013 mbar air (Sørensen et al. 2003).
- (c) HO radicals generated by the photolysis of  $\text{O}_3$  at 254 nm in the presence of  $\text{H}_2$ . The concentrations of  $\text{CH}_4$  and  $\text{CH}_3\text{F}$  were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CH}_3\text{F})/k(\text{HO}+\text{CH}_4)=2.30\pm 0.11$  was placed on an absolute basis by using  $k(\text{HO}+\text{CH}_4)=6.14\times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 296 K (IUPAC, current recommendation).
- (d) HO radicals generated by the photolysis of  $\text{O}_3$  at 254 nm in the presence of  $\text{H}_2$ . The decay of  $\text{CH}_4$  and  $\text{CH}_3\text{F}$  concentrations was monitored by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CH}_3\text{F})/k(\text{HO}+\text{CH}_4)=2.2\pm 0.2$  was placed on an absolute basis by using  $k(\text{HO}+\text{CH}_4)=6.01\times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 295 K (IUPAC, current recommendation).
- (e) HO radicals were generated by the photolysis of  $\text{H}_2\text{O}$  at 185 nm or of  $\text{O}_3\text{-H}_2\text{O}$  mixtures in the UV in  $\text{H}_2\text{O}$  (or  $\text{O}_3\text{-H}_2\text{O}$ )- $\text{CH}_3\text{F-CH}_3\text{CHF}_2\text{-O}_2\text{-N}_2$  mixtures. The concentrations of  $\text{CH}_3\text{F}$  and  $\text{CH}_3\text{CHF}_2$  were measured by IR spectroscopy. The

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measured rate coefficient ratio of  $k(\text{HO}+\text{CH}_3\text{F})/k(\text{HO}+\text{CH}_3\text{CHF}_2)=(0.99\pm 0.10)\exp[-(174\pm 34)/T]$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+\text{CH}_3\text{CHF}_2)=2.80\times 10^{-18}T^2\exp(-580/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  (IUPAC, current recommendation).

(f) HO radicals generated by the photolysis of  $\text{O}_3$  at 254 nm in the presence of  $\text{H}_2\text{O}$  vapour. The decay of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{F}$  concentrations was monitored by FTIR spectroscopy. The rate coefficient ratio of  $k(\text{HO}+\text{CH}_3\text{F})/k(\text{HO}+\text{CH}_3\text{Cl})=(0.97\pm 0.23)\exp[-(156\pm 82)/T]$  was measured over the temperature range 308–393 K. The rate coefficient ratio was placed on an absolute basis by using  $k(\text{HO}+\text{CH}_3\text{Cl})=4.34\times 10^{-18}T^2\exp(-700/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

$k=2.1\times 10^{-14}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  at 298 K.

$k=1.9\times 10^{-12}\exp(-1350/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  over the temperature range 240–300 K.

### Reliability

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

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

### Comments on Preferred Values

The absolute rate coefficients of Schmoltnner 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

Schmoltnner 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 Schmoltnner et al. (1993), Hsu and DeMore (1995) and DeMore (1996). Because secondary reactions of HO radicals with CH<sub>2</sub>F 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 Mögelberg 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), Schmoltnner 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  $k = 3.66 \times 10^{-18} T^2 \exp(-818/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 243–393 K. The preferred Arrhenius expression,  $k=A \exp(-B/T)$ , is centered at 265 K and is derived from the three parameter equation with  $A=C e^2 T^2$  and  $B=D + 2T$ .

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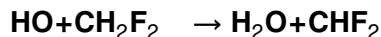
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## IV.A1.11



$$\Delta H^\circ = -65.0 \text{ kJ mol}^{-1}$$

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(7.8 \pm 1.2) \times 10^{-15}$	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	Schmoltnner et al., 1993	PLP/FP-LIF
$(1.09 \pm 0.03) \times 10^{-14}$	298		
$(1.00 \pm 0.03) \times 10^{-14}$	298	Szilagyí et al., 2000	DF-RF
<i>Relative Rate Coefficients</i>			
$2.24 \times 10^{-18} T^2 \exp[-(857 \pm 24)/T]$	297–383	Hsu and DeMore, 1995	RR (b)
$1.12 \times 10^{-14}$	297		

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## 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<sub>2</sub>O at 185 nm or of O<sub>3</sub>-H<sub>2</sub>O mixtures in the UV in H<sub>2</sub>O (or O<sub>3</sub>-H<sub>2</sub>O)-CH<sub>2</sub>F<sub>2</sub>-CH<sub>3</sub>CHF<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures. The concentrations of CH<sub>2</sub>F<sub>2</sub> and CH<sub>3</sub>CHF<sub>2</sub> were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CH}_2\text{F}_2)/k(\text{HO}+\text{CH}_3\text{CHF}_2)=(0.80\pm 0.06)\exp[-(277\pm 24)/T]$  is placed on an absolute basis using a rate coefficient of  $k(\text{HO}+\text{CH}_3\text{CHF}_2)=2.80 \times 10^{-18} T^2 \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

## Preferred Values

$k=1.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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

## Reliability

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

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

## Comments on Preferred Values

The absolute rate coefficients of Schmoltnner 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),

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Jeong and Kaufman (1982), Jeong et al. (1984), Talukdar et al. (1991) and Schmoltnner 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), Schmoltnner et al. (1993), and Szilagyi et al. (2000) have been fitted to the three parameter equation  $k = CT^2 \exp(-D/T)$ , resulting in  $k = 4.80 \times 10^{-18} T^2 \exp(-1080/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 222–492 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 255 K and is derived from the three-parameter equation with  $A = Ce^{2T^2}$  and  $B = D + 2T$ .

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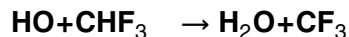
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## IV.A1.12



$$\Delta H^\circ = -47.5 \text{ kJ mol}^{-1}$$

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.0 \pm 0.2) \times 10^{-16}$	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
$2.98 \times 10^{-12} \exp[-(2908 \pm 156)/T]$	387–480	Jeong et al., 1984	DF-RF (a)
$1.71 \times 10^{-16}$	298		(b)
$(2.3 \pm 0.4) \times 10^{-15}$	298	Bera and Hanrahan, 1988	PR-RA
$6.93 \times 10^{-13} \exp[-(2300 \pm 100)/T]$	252–374	Schmoltner et al., 1993	FP-LIF
$(3.08 \pm 0.28) \times 10^{-16}$	298		
$1.1 \times 10^{-12} \exp[-(2300 \pm 207)/T]$	298–753	Medhurst et al., 1997	PLP-LIF
$(1.5 \pm 0.2) \times 10^{-16}$	298		

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$1.05 \times 10^{-18} T^2 \exp[-(1774 \pm 44)/T]$	298–383	Hsu and DeMore, 1995	RR (c)
$2.42 \times 10^{-16}$	298		
$6.19 \times 10^{-19} T^2 \exp[-(1523 \pm 34)/T]$	253–343	Chen et al., 2003	RR (d,e)
$3.32 \times 10^{-16}$	298		
$1.12 \times 10^{-18} T^2 \exp[-(1706 \pm 44)/T]$	253–343	Chen et al., 2003	RR (d,f)
$3.25 \times 10^{-16}$	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<sub>2</sub>O at 185 nm or of O<sub>3</sub>-H<sub>2</sub>O mixtures in the UV in H<sub>2</sub>O (or H<sub>2</sub>O-O<sub>3</sub>)-CHF<sub>3</sub>-CHF<sub>2</sub>CF<sub>3</sub>-N<sub>2</sub>-O<sub>2</sub> mixtures. The concentrations of CHF<sub>3</sub> and CHF<sub>2</sub>CF<sub>3</sub> were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CHF}_3)/k(\text{HO}+\text{CHF}_2\text{CF}_3)=(1.14 \pm 0.08) \exp[-(654 \pm 44)/T]$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+\text{CHF}_2\text{CF}_3)=9.24 \times 10^{-19} T^2 \exp(-1120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(d) Relative rate method. HO radicals were generated from the photolysis of H<sub>2</sub>O at 254 nm in the presence of a continuous flow of a 3% O<sub>3</sub> in O<sub>2</sub> mixture. The concentrations of CHF<sub>3</sub> and reference compounds were measured by GC-FID.

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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  $\text{CHF}_2\text{CF}_3$ . An Arrhenius plot of the Chen et al. (2003) data gives a rate coefficient ratio of  $k(\text{HO}+\text{CHF}_3)/k(\text{HO}+\text{CHF}_2\text{CF}_3)=(0.67\pm 0.12)\exp[-(403\pm 34)/T]$  over the temperature range 253–343 K. The rate coefficient ratio was placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+\text{CF}_3\text{CHF}_2)=9.24\times 10^{-19}T^2\exp(-1120/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  (IUPAC, current recommendation).

(f) Relative to  $\text{CHF}_2\text{Cl}$ . An Arrhenius plot of the Chen et al. (2003) data gives a rate coefficient ratio of  $k(\text{HO}+\text{CHF}_3)/k(\text{HO}+\text{CHF}_2\text{Cl})=(0.74\pm 0.17)\exp[-(706\pm 44)/T]$  over the temperature range 253–343 K. The rate coefficient ratio was placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+\text{CHF}_2\text{Cl})=1.52\times 10^{-18}T^2\exp(-1000/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

$k=2.7\times 10^{-16}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  at 298 K.

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

### Reliability

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

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

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## 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 ~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 ~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  $k = 1.42 \times 10^{-18} T^2 \exp(-1798/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 252–480 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 270 K and is obtained from the three parameter equation with  $A = Ce^{2T^2}$  and  $B = D + 2T$ . The relative rate data of Hsu and DeMore (1995) are ~10% lower than the preferred values.

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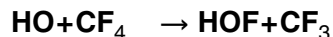
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#### IV.A1.13



$$\Delta H^\circ = 327.2 \text{ kJ mol}^{-1}$$

#### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<4 \times 10^{-16}$	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 Schmoltnner et al. (1993) for HO radical reaction rate coefficient measurements with related hydrofluorocarbons.

#### Preferred Values

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

#### Comments on Preferred Values

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

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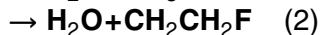
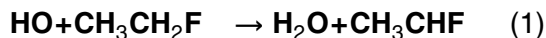
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#### IV.A1.14



$$\Delta H^\circ(1) = -74.4 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -59.6 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.32 \pm 0.37) \times 10^{-13}$	297 ± 2	Nip et al., 1979	FP-RA
$2.69 \times 10^{-12} \exp[-(750 \pm 100)/T]$	243–373	Schmoltnner 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		
<i>Relative Rate Coefficients</i>			
$1.73 \times 10^{-17} T^2 \exp[-(657 \pm 36)/T]$	285–364	Hsu and DeMore, 1995	RR (a)
$1.69 \times 10^{-13}$	298		

#### Comments

(a) HO radicals were generated by the photolysis of H<sub>2</sub>O at 185 nm or of H<sub>2</sub>O-O<sub>3</sub> mixtures in the UV in H<sub>2</sub>O (or H<sub>2</sub>O-O<sub>3</sub>)-CH<sub>3</sub>CH<sub>2</sub>F-C<sub>2</sub>H<sub>6</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures. The concentrations of CH<sub>3</sub>CH<sub>2</sub>F and C<sub>2</sub>H<sub>6</sub> were measured by FTIR spectroscopy. The

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measured rate coefficient ratio of  $k(\text{HO}+\text{CH}_3\text{CH}_2\text{F})/k(\text{HO}+\text{C}_2\text{H}_6)=(1.16 \pm 0.13) \exp[-(158 \pm 36)/T]$  is placed on an absolute basis using a rate coefficient of  $k(\text{HO}+\text{C}_2\text{H}_6)=1.49 \times 10^{-17} T^2 \exp(-499/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

## 5 Preferred Values

$k=2.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k=2.7 \times 10^{-12} \exp(-765/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 210–300 K.

$k_1/k=0.85 \text{ K}$ .

## Reliability

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

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

$k_1/k = \pm 0.15$  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

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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<sub>2</sub>F 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<sub>3</sub>) 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  $k = 6.12 \times 10^{-18} T^2 \exp(-275/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 210–480 K. The preferred Arrhenius expression  $k = A \exp(-B/T)$  is centered at 245 K and is derived from the three parameter equation with  $A = Ce^{2T^2}$  and  $B = D + 2T$ . 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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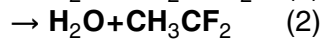
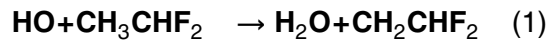
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## IV.A1.15



$$\Delta H^\circ(1) = -53.8 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -69.8 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.12 \pm 0.70) \times 10^{-14}$	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
$4.2 \times 10^{-14}$	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		

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(3.86 \pm 0.67) \times 10^{-14}$	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)
$3.02 \times 10^{-14}$	298		
$1.18 \times 10^{-20} T^{2.82} \exp[-(388 \pm 67)/T]$	298–358	Hsu and DeMore, 1995	RR (b)
$3.05 \times 10^{-14}$	298		
$2.53 \times 10^{-18} T^2 \exp[-(557 \pm 19)/T]$	286–403	Wilson et al., 2003	RR (d,e)
$3.47 \times 10^{-14}$	298		
$1.22 \times 10^{-18} T^2 \exp[-(329 \pm 42)/T]$	290–391	Wilson et al., 2003	RR (d,f)
$3.59 \times 10^{-14}$	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<sub>2</sub>O at 185 nm in H<sub>2</sub>O-CH<sub>3</sub>CHF<sub>2</sub>-C<sub>2</sub>H<sub>6</sub>-N<sub>2</sub>-O<sub>2</sub> mixtures. The concentrations of CH<sub>3</sub>CHF<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CH}_3\text{CHF}_2)/k(\text{HO}+\text{C}_2\text{H}_6)=0.161 \pm 0.028$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO}+\text{C}_2\text{H}_6)=2.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of H<sub>2</sub>O at 185 nm or of O<sub>3</sub>-H<sub>2</sub>O mixtures in H<sub>2</sub>O (or O<sub>3</sub>-H<sub>2</sub>O)-CH<sub>3</sub>CHF<sub>2</sub>-CH<sub>4</sub>-N<sub>2</sub>-O<sub>2</sub> mixtures. The concentrations of CH<sub>3</sub>CHF<sub>2</sub> and CH<sub>4</sub> were measured by FTIR spectroscopy. The measured



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rate coefficient ratios of  $k(\text{HO}+\text{CH}_3\text{CHF}_2)/k(\text{HO}+\text{CH}_4)=5.2\pm 0.5$  (DeMore, 1992) and  $k(\text{HO}+\text{CH}_3\text{CHF}_2)/k(\text{HO}+\text{CH}_4)=(0.64\pm 0.13) \exp[(599\pm 67)/T]$  (Hsu and DeMore, 1995) are placed on an absolute basis by use of a rate coefficient of  $k(\text{HO}+\text{CH}_4)=1.85\times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(c) HO radicals were generated by the photolysis of  $\text{H}_2\text{O}$  at 185 nm or of  $\text{O}_3\text{-H}_2\text{O}$  mixtures in the UV in  $\text{H}_2\text{O}$  (or  $\text{H}_2\text{O-O}_3$ )- $\text{CH}_3\text{CHF}_2$ - $\text{CH}_3\text{CCl}_3$ - $\text{O}_2$ - $\text{N}_2$  mixtures. The concentrations of  $\text{CH}_3\text{CHF}_2$  and  $\text{CH}_3\text{CCl}_3$  were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CH}_3\text{CHF}_2)/k(\text{HO}+\text{CH}_3\text{CCl}_3) = (1.53\pm 0.28) \exp[(220\pm 57)/T]$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO}+\text{CH}_3\text{CCl}_3)=2.25\times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(d) Relative rate method. HO radicals were generated by photolyzing  $\text{H}_2\text{O}$  vapor at 185 nm. Reactant and reference compound concentrations were monitored by GC/MS.

(e) Relative to  $\text{C}_2\text{H}_6$ . An Arrhenius plot of the data gives the temperature dependence of the measured ratios as  $(0.17 \pm 0.01) \exp[-(58\pm 19)/T]$ , which is placed on an absolute basis using a rate coefficient of  $k(\text{HO}+\text{C}_2\text{H}_6)=1.49 \times 10^{-17} T^2 \exp(-499/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(f) Relative to cyclopropane. An Arrhenius plot of the data gives the temperature dependence of the measured ratios as  $(0.29 \pm 0.10) \exp[(125\pm 42)/T]$ , which is placed on an absolute basis using a rate coefficient of  $k(\text{HO}+\text{cyclo-C}_3\text{H}_6)=4.21 \times 10^{-18} T^2 \exp(-454/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson, 2003).

(g) Relative rate method. HO radicals were generated by the UV photolysis of  $\text{CH}_3\text{ONO}$  in the presence of the reactant in 700 Torr total pressure of air diluent. Reference compound concentrations were monitored by FTIR.  $\text{CH}_3\text{CHF}_2$  loss was measured indirectly from the observed formation of  $\text{COF}_2$ .

(h) Relative to C<sub>2</sub>H<sub>4</sub>. The measured rate coefficient ratio of  $k(\text{CH}_3\text{CHF}_2+\text{HO})/k(\text{C}_2\text{H}_4+\text{HO})=(3.59\pm 0.27)\times 10^{-3}$  placed on an absolute basis by using a rate coefficient of  $k(\text{C}_2\text{H}_4+\text{HO})=8.7\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 295 K (Calvert et al., 2000).

5 (i) Relative to C<sub>2</sub>H<sub>2</sub>. The measured rate coefficient ratio of  $k(\text{CH}_3\text{CHF}_2+\text{HO})/k(\text{C}_2\text{H}_2+\text{HO})=(3.58\pm 0.12)\times 10^{-2}$  is placed on an absolute basis by using a rate coefficient of  $k(\text{C}_2\text{H}_2+\text{HO})=8.45\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 296 K (Sørensen et al., 2003).

### Preferred Values

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

### Reliability

$\Delta\log k = \begin{matrix} +0.10 \\ -0.20 \end{matrix}$  at 298 K.  
15  $\Delta(E/R) = \begin{matrix} +200 \\ -400 \end{matrix}$  K.

### Comments on Preferred Values

20 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,

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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<sub>2</sub>H<sub>6</sub> 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<sub>2</sub>H<sub>6</sub>. 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<sub>2</sub>H<sub>6</sub> were used in the evaluation. The relative rate coefficients of DeMore (1992) relative to C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub> 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<sub>2</sub>H<sub>6</sub>. 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<sub>2</sub>H<sub>6</sub>.

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<sub>2</sub>H<sub>6</sub>) 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 at 245 K and is derived from the three-parameter equation with  $A = C e^{2T^2}$  and  $B = D + 2T$ . 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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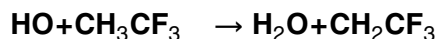
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## IV.A1.16



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

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.92 \pm 1.20) \times 10^{-11} \exp[-(3200 \pm 500)/T]$	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		
<i>Relative Rate Coefficients</i>			
$7.96 \times 10^{-21} T^{2.82} \exp[-(1210 \pm 90)/T]$	298–403	Hsu and DeMore, 1995	RR (c,d)
$1.30 \times 10^{-15}$	298		
$2.00 \times 10^{-18} T^2 \exp[-(1490 \pm 21)/T]$	298–383	Hsu and DeMore, 1995	RR (c,e)
$1.20 \times 10^{-15}$	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.

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(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<sub>2</sub>O at 185 nm or of O<sub>3</sub>-H<sub>2</sub>O mixtures in the UV in H<sub>2</sub>O (or O<sub>3</sub>-H<sub>2</sub>O)-CH<sub>3</sub>CF<sub>3</sub>-CH<sub>4</sub> (or CHF<sub>2</sub>CF<sub>3</sub>)-O<sub>2</sub>-N<sub>2</sub> mixtures. The concentrations of CH<sub>3</sub>CF<sub>3</sub> and CH<sub>4</sub> (or CHF<sub>2</sub>CF<sub>3</sub>) were measured by FTIR spectroscopy.

(d) The measured rate coefficient ratio  $k(\text{HO}+\text{CH}_3\text{CF}_3)/k(\text{HO}+\text{CH}_4)=(0.43\pm 0.12)\exp[(-223\pm 90)/T]$  was placed on an absolute basis by use of the rate coefficient  $k(\text{HO}+\text{CH}_4)=1.85\times 10^{-20} T^{2.82}\exp(-987/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation).

(e) The measured rate coefficient ratio  $k(\text{HO}+\text{CH}_3\text{CF}_3)/k(\text{HO}+\text{CHF}_2\text{CF}_3)=(2.16\pm 0.14)\exp[-(370\pm 21)/T]$  was placed on an absolute basis by use of the rate coefficient  $k(\text{HO}+\text{CHF}_2\text{CF}_3)=9.24\times 10^{-19} T^2\exp(-1120/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

$k=1.2\times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

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

### Reliability

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

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

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## 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<sub>4</sub> and CHF<sub>2</sub>CF<sub>3</sub>, 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  $k = 1.91 \times 10^{-18} T^2 \exp(-1456/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 223–403 K. The preferred Arrhenius expression  $k = A \exp(-B/T)$ , is centered at 255 K and is derived from the three parameter equation with  $A = C e^2 T^2$  and  $B = D + 2T$ . 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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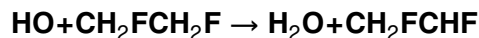
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## IV.A1.17



$$\Delta H^\circ = -69.5 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.12 \pm 0.12) \times 10^{-13}$	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		
<i>Relative Rate Coefficients</i>			
$4.77 \times 10^{-18} T^2 \exp[-(454 \pm 23)/T]$	293–397	Wilson et al., 2003	RR (a,b)
$9.23 \times 10^{-14}$	298		
$2.15 \times 10^{-18} T^2 \exp[-(188 \pm 29)/T]$	287–409	Wilson et al., 2003	RR (a,c)
$1.02 \times 10^{-13}$	298		
$4.68 \times 10^{-18} T^2 \exp[-(441 \pm 16)/T]$	292–393	Wilson et al., 2003	RR (a,d)
$9.46 \times 10^{-14}$	298		

### Comments

- (a) Relative rate method. HO radicals were generated by photolyzing H<sub>2</sub>O vapor at 185 nm. Reactant and reference compound concentrations were monitored by GC/MS.

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(b) Relative to C<sub>2</sub>H<sub>6</sub>. 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  $k(\text{HO} + \text{C}_2\text{H}_6) = 1.49 \times 10^{-17} T^2 \exp(-499/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (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  $k(\text{HO} + \text{cyclopropane}) = 4.21 \times 10^{-18} T^2 \exp(-454/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson, 2003).

(d) Relative to CH<sub>3</sub>CHF<sub>2</sub>. 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  $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 2.80 \times 10^{-18} T^2 \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

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

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

### Reliability

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

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

### 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<sub>2</sub>H<sub>6</sub> and CH<sub>2</sub>FCH<sub>2</sub>F) are in good agreement

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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<sub>2</sub>H<sub>6</sub> and CH<sub>3</sub>CHF<sub>2</sub>). 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<sub>2</sub>H<sub>6</sub> and CH<sub>3</sub>CHF<sub>2</sub> have been fitted to the three parameter equation  $k=CT^2 \exp(-D/T)$  resulting in  $k=3.39 \times 10^{-18} T^2 \exp(-312/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 210–480 K. The preferred Arrhenius expression,  $k=A \exp(-B/T)$ , is centered at 245 K and is derived from the three-parameter equation with  $A=Ce^2 T^2$  and  $B=D+2T$ .

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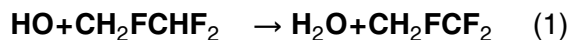
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## IV.A1.18



$$\Delta H^\circ(1) = -78.0 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -80.1 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.48 \times 10^{-12} \exp[-(1000 \pm 100)/T]$	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
<i>Relative Rate Coefficients</i>			
$4.97 \times 10^{-18} T^2 \exp[-1012/T]$	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  $\text{O}_3$  in the presence of water vapor at  $\sim 250 \text{ nm}$  at atmospheric pressure of air. Irradiations of  $\text{O}_3\text{-H}_2\text{O-CH}_2\text{FCHF}_2\text{-CH}_3\text{CCl}_3\text{-air}$  mixtures were carried out and the concentrations of  $\text{CH}_2\text{FCHF}_2$  and  $\text{CH}_3\text{CCl}_3$  measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CH}_2\text{FCHF}_2)/k(\text{HO} + \text{CH}_3\text{CCl}_3) = 2.21 \exp(-102/T)$  is placed on an

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absolute basis by use of a rate coefficient of  $k(\text{HO}+\text{CH}_3\text{CCl}_3)=2.25\times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

$k=1.5\times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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

### Reliability

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

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

### Comments on Preferred Values

10 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 ( $k=4.97\times 10^{-18} T^2 \exp(-1012/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature  
15 range 278–323 K) and is centered at 300 K with  $A=Ce^2 T^2$  and  $B=D+2T$ .

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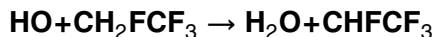
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$$\Delta H^\circ = -63.1 \text{ kJ mol}^{-1}$$

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.2 \times 10^{-12} \exp[-(1800 \pm 200)/T]$	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
$1.1 \times 10^{-12} \exp[-(1424 \pm 35)/T]$	294–473	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
$6.25 \times 10^{-15}$	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

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$8.26 \times 10^{-21} T^{2.82} \exp [-(905 \pm 115)/T]$	298–358	DeMore, 1993	RR (b,c)
$3.76 \times 10^{-15}$	298		
$1.84 \times 10^{-18} T^2 \exp [-(1129 \pm 44)/T]$	298–358	DeMore, 1993	RR (b,d)
$3.70 \times 10^{-15}$	298		
$1.93 \times 10^{-18} T^2 \exp [-(1132 \pm 79)/T]$	298–358	DeMore, 1993	RR (b,e)
$3.84 \times 10^{-15}$	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<sub>3</sub>-H<sub>2</sub>O-O<sub>2</sub>-Ar mixtures at 254 nm. The CH<sub>2</sub>FCF<sub>3</sub>, CH<sub>4</sub>, CH<sub>3</sub>CCl<sub>3</sub>, and CHF<sub>2</sub>CF<sub>3</sub> concentrations were monitored during the experiments by FTIR absorption spectroscopy. The measured rate coefficient ratios of  $k(\text{HO}+\text{CH}_4)/k(\text{HO}+\text{CH}_2\text{FCF}_3)=(2.24 \pm 0.78) \exp [-(82 \pm 115)/T]$ ,  $k(\text{HO}+\text{CH}_3\text{CCl}_3)/k(\text{HO}+\text{CH}_2\text{FCF}_3)=(1.22 \pm 0.17) \exp [(219 \pm 44)/T]$  and  $k(\text{HO}+\text{CHF}_2\text{CF}_3)/k(\text{HO}+\text{CH}_2\text{FCF}_3)=(0.48 \pm 0.12) \exp [(12 \pm 79)/T]$  are placed on an absolute basis by use of rate coefficients  $k(\text{HO}+\text{CH}_4)=1.85 \times 10^{-20} T^{2.82} \exp (-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation),  $k(\text{HO}+\text{CH}_3\text{CCl}_3)=2.25 \times 10^{-18} T^2 \exp (-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, cur-

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rent recommendation) and  $k(\text{HO}+\text{CHF}_2\text{CF}_3)=9.24\times 10^{-19} T^2 \exp(-1120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(c) Relative to  $k(\text{HO}+\text{CH}_4)$ .

(d) Relative to  $k(\text{HO}+\text{CH}_3\text{CCl}_3)$ .

(e) Relative to  $k(\text{HO}+\text{CHF}_2\text{CF}_3)$ .

(f) Relative rate method. HO radicals were generated by the photolysis of  $\text{O}_3$  at  $\sim 250 \text{ nm}$  in the presence of water vapor at atmospheric pressure of air. Irradiations of  $\text{O}_3\text{-H}_2\text{O-CH}_2\text{FCF}_3\text{-CH}_3\text{CCl}_3\text{-air}$  mixtures were carried out at  $298\pm 2 \text{ K}$  and the concentrations of  $\text{CH}_2\text{FCF}_3$  and  $\text{CH}_3\text{CCl}_3$  measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CH}_2\text{FCF}_3)/k(\text{HO}+\text{CH}_3\text{CCl}_3)=0.41\pm 0.05$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+\text{CH}_3\text{CCl}_3)=9.5\times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $298 \text{ K}$  (IUPAC, current recommendation).

(g) Relative rate method. HO radicals were generated by the photolysis of  $\text{O}_3$  in the presence of water vapor. Irradiations of  $\text{O}_3\text{-H}_2\text{O-CH}_2\text{FCF}_3\text{-CH}_2\text{FCHF}_2\text{-air}$  mixtures were carried out at  $298\pm 2 \text{ K}$  and the concentrations of  $\text{CH}_2\text{FCF}_3$  and  $\text{CH}_2\text{FCHF}_2$  measured by GC and FTIR spectroscopy. The measured rate coefficient ratio  $k(\text{HO}+\text{CH}_2\text{FCHF}_2)/k(\text{HO}+\text{CH}_2\text{FCF}_3)=3.58\pm 0.16$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+\text{CH}_2\text{FCF}_3)=1.5\times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $298 \text{ K}$  (IUPAC, current recommendation).

### Preferred Values

$k=4.6\times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $298 \text{ K}$ .

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

## Reliability

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

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

## Comments on Preferred Values

5 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.

20 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  $k = 1.0 \times 10^{-18} T^2 \exp(-885/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220–460 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 255 K and is derived from the three-parameter equation with  $A = Ce^2 T^2$  and  $B = D + 2T$ . This expression yields rate coefficients that are 10–15% higher than those calculated from the

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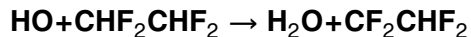
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## IV.A1.20



$$\Delta H^\circ = -58.41 \text{ kJ mol}^{-1}$$

### Rate coefficient data

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

### Comments

(a) HO radicals were generated by the photolysis of  $\text{O}_3\text{-H}_2\text{O-O}_2\text{-Ar}$  mixtures at 254 nm. The concentrations of  $\text{CHF}_2\text{CHF}_2$  and  $\text{CH}_3\text{CCl}_3$  were measured during the experiments by FTIR absorption spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CH}_3\text{CCl}_3)/k(\text{HO} + \text{CHF}_2\text{CHF}_2) = (0.84 \pm 0.10) \exp[(212 \pm 37)/T]$  is placed on an absolute basis by use of a rate coefficient of

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$k(\text{HO}+\text{CH}_3\text{CCl}_3)=2.25\times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of  $\text{O}_3\text{-H}_2\text{O-O}_2\text{-Ar}$  mixtures at 254 nm. The concentrations of  $\text{CHF}_2\text{CHF}_2$  and  $\text{CH}_2\text{FCF}_3$  were measured during the irradiations by FTIR absorption spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CH}_2\text{FCF}_3)/k(\text{HO}+\text{CHF}_2\text{CHF}_2)=(0.85\pm 0.07) \exp[-(80\pm 25)/T]$  is placed on an absolute basis by use of the rate coefficient  $k(\text{HO}+\text{CH}_2\text{FCF}_3)=1.0\times 10^{-18} T^2 \exp(-885/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(c) HO radicals were generated by irradiation of  $\text{O}_3\text{-H}_2\text{O-O}_2\text{-Ar}$  mixtures at 254 nm. The concentrations of  $\text{CHF}_2\text{CHF}_2$  and  $\text{CHF}_2\text{CF}_3$  were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CHF}_2\text{CF}_3)/k(\text{HO}+\text{CHF}_2\text{CHF}_2)=(0.48\pm 0.11) \exp[-(109\pm 77)/T]$  is placed on an absolute basis by use of the rate coefficient  $k(\text{HO}+\text{CHF}_2\text{CF}_3)=9.24 \times 10^{-19} T^2 \exp(-1120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

$k=6.1\times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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

### Reliability

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

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

## 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  $k = 1.80 \times 10^{-18} T^2 \exp(-974/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290–360 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 320 K and is derived from the three-parameter expression with  $A = Ce^2 T^2$  and  $B = D + 2T$ .

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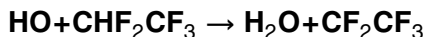
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## IV.A1.21



$$\Delta H^\circ = -54.1 \text{ kJ mol}^{-1}$$

### Rate coefficient data

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

### Comments

(a) HO radicals were generated by the photolysis of O<sub>3</sub> in the presence of water vapor at 254 nm. Irradiations of O<sub>3</sub>-H<sub>2</sub>O-CHF<sub>2</sub>CF<sub>3</sub>-CH<sub>4</sub>-O<sub>2</sub>-N<sub>2</sub> (or Ar) mixtures were carried out, and the concentrations of CHF<sub>2</sub>CF<sub>3</sub> and the CH<sub>4</sub> were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio  $k(\text{HO} + \text{CH}_4)/k(\text{HO} + \text{CF}_3\text{CHF}_2) = 3.9 \pm 0.5$  is placed on an absolute basis by use of

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the rate coefficient  $k(\text{HO}+\text{CH}_4)=6.4\times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K (IUPAC, current recommendation).

### Preferred Values

$k=1.9\times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

5  $k=4.4\times 10^{-13}\exp(-1630/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 220–300 K.

### Reliability

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

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

### Comments on Preferred Values

10 The relatively high results of Clyne and Holt (1979) and Brown et al. (1990) suggest the presence of reactive impurities in the  $\text{CHF}_2\text{CF}_3$  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).  
15 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  $k=9.24\times 10^{-19}T^2\exp(-1120/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 220–360 K. The preferred Arrhenius expression,  $k=A\exp(-B/T)$ , is centered at 255 K and is derived from the three parameter equation with  $A=Ce^{2T^2}$   
20 and  $B=D+2T$ .

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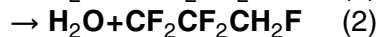
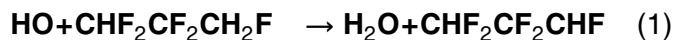
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## IV.A1.22



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

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

### 5 Comments

(a) Relative rate method. HO radicals were generated by the photolysis of  $\text{H}_2\text{O}$  at 185 nm or of  $\text{O}_3\text{-H}_2\text{O}$  mixtures in the UV in  $\text{H}_2\text{O}$  (or  $\text{H}_2\text{O-O}_3$ )- $\text{CHF}_2\text{CF}_2\text{CH}_2\text{F-CH}_4\text{-O}_2\text{-N}_2$  mixtures. The concentrations of  $\text{CHF}_2\text{CF}_2\text{CH}_2\text{F}$  and  $\text{CH}_4$  were measured by FTIR absorption spectroscopy. The measured rate coefficient of  $k(\text{HO} + \text{CHF}_2\text{CF}_2\text{CH}_2\text{F})/k(\text{HO} + \text{CH}_4) = (0.67 \pm 0.07) \exp[(164 \pm 34)/T]$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{CH}_4) = 1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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## Preferred Values

$k = 7.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 2.2 \times 10^{-12} \exp(-1685/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 285–365 K.

## Reliability

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

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

## Comments on Preferred Values

10 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  $k = 2.84 \times 10^{-18} T^2 \exp(-1045/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 285–  
15 365 K. The preferred Arrhenius expression,  $k = A \exp(B/T)$ , is centered at 320 K and is derived from the three parameter equation,  $k = CT^2 \exp(D/T)$  with  $A = Ce^2 T^2$  and  $B = D + 2T$ .

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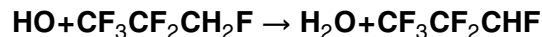
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## IV.A1.23



### Rate coefficient data

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

### 5 Preferred Values

$k = 6.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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

### Reliability

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

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

### Comments on Preferred Values

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

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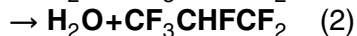
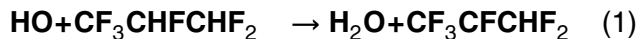
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#### IV.A1.24



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

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

#### 5 Comments

(a) HO radicals were generated by the photolysis of  $\text{H}_2\text{O}$  at 185 nm or of  $\text{O}_3\text{-H}_2\text{O}$  mixtures in the UV, in  $\text{H}_2\text{O}$  (or  $\text{O}_3\text{-H}_2\text{O}$ )- $\text{CF}_3\text{CHFCHF}_2\text{-CH}_4\text{-O}_2\text{-N}_2$  mixtures. The concentrations of  $\text{CF}_3\text{CHFCHF}_2$  and  $\text{CH}_4$  were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CF}_3\text{CHFCHF}_2)/k(\text{HO} + \text{CH}_4) = (0.36 \pm 0.01) \exp[(231 \pm 12)/T]$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO} + \text{CH}_4) = 1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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## Preferred Values

$k=5.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k=1.4 \times 10^{-12} \exp(-1680/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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  $k=1.76 \times 10^{-18} T^2 \exp(-1021/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 294–380 K. The preferred Arrhenius expression,  $k=A \exp(-B/T)$ , is centered at 330 K and is derived from the three parameter equation,  $k=A \exp(-B/T)$  with  $A=Ce^2 T^2$  and  $B=D + 2T$ . 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.

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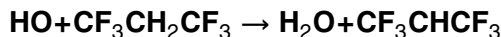
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.0 \times 10^{-14} \exp[-(906 \pm 151)/T]$	257–311	Garland et al., 1993	PLP-LIF
$9.6 \times 10^{-16}$	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		
<i>Relative Rate Coefficients</i>			
$1.16 \times 10^{-18} T^2 \exp[-(1700 \pm 109)/T]$	298–367	Hsu and DeMore, 1995	RR (a)
$3.43 \times 10^{-16}$	298		
$(3.5 \pm 1.5) \times 10^{-16}$	298	Barry et al., 1997	RR (b)

## 5 Comments

(a) Relative rate method. HO radicals were generated from the photolysis of H<sub>2</sub>O at 185 nm or of O<sub>3</sub>-H<sub>2</sub>O mixtures in the UV in H<sub>2</sub>O (or O<sub>3</sub>-H<sub>2</sub>O)-CF<sub>3</sub>CH<sub>2</sub>CF<sub>3</sub>-CHF<sub>2</sub>CF<sub>3</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures. The concentrations of CF<sub>3</sub>CH<sub>2</sub>CF<sub>3</sub> and CHF<sub>2</sub>CF<sub>3</sub> were measured by FTIR absorption spectroscopy. The measured rate coefficient

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ratio of  $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CF}_3)/k(\text{HO}+\text{CHF}_2\text{CF}_3)=(1.26\pm 0.41)\exp[-(580\pm 109)/T]$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+\text{CHF}_2\text{CF}_3)=9.24\times 10^{-19}T^2\exp(-1120/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  (IUPAC, current recommendation).

(b) Relative rate method. HO radicals were generated by UV photolysis of  $\text{O}_3$  at 254 nm in the presence of  $\text{H}_2\text{O}$  vapour. Mixtures of  $\text{O}_3/\text{CF}_3\text{CH}_2\text{CF}_3/\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3/\text{H}_2\text{O}$  were photolysed in air at 298 K,  $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CF}_3)/k(\text{HO}+\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3)$  was found to be  $0.06\pm 0.02$ . Using the experimentally derived value of  $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3)=2.0\times 10^{-12}\exp[-(1750\pm 400)/T]\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  gives  $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CF}_3)=(3.5\pm 1.5)\times 10^{-16}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ .

### Preferred Values

$k=3.3\times 10^{-16}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  at 298 K.

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

### Reliability

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

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

### 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

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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  $k=1.91 \times 10^{-18} T^2 \exp(-1865/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 273–413 K. The preferred Arrhenius expression,  $k=A \exp(-B/T)$ , is centered at 300 K and is derived from the three-parameter equation with  $A=Ce^2 T^2$  and  $B=D + 2T$ . 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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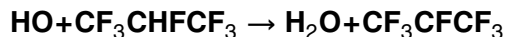
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## Rate coefficient data

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

## 5 Comments

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

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(b) Relative rate method. HO radicals were generated by the photolysis of H<sub>2</sub>O at 185 nm or O<sub>3</sub> at 254 nm, in H<sub>2</sub>O (or O<sub>3</sub>-H<sub>2</sub>O) – CF<sub>3</sub>CHF<sub>2</sub>CF<sub>3</sub> – CH<sub>4</sub> (or CHF<sub>2</sub>CF<sub>3</sub>)-O<sub>2</sub> - N<sub>2</sub> mixtures. The concentrations of CF<sub>3</sub>CHF<sub>2</sub>CF<sub>3</sub> and CH<sub>4</sub> (or CHF<sub>2</sub>CF<sub>3</sub>) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratios of  $k(\text{HO}+\text{CF}_3\text{CHF}_2\text{CF}_3)/k(\text{HO}+\text{CH}_4)=(0.17\pm 0.05) \exp[(117 \pm 105)/T]$  and  $k(\text{HO}+\text{CF}_3\text{CHF}_2\text{CF}_3)/k(\text{HO}+\text{CHF}_2\text{CF}_3)=(0.83\pm 0.22) \exp[(38\pm 89)/T]$  are placed on an absolute basis by use of rate coefficients of  $k(\text{HO}+\text{CH}_4)=1.85\times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation) and  $k(\text{HO}+\text{CHF}_2\text{CF}_3)=9.24\times 10^{-19} T^2 \exp(-1120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(c) Relative to  $k(\text{HO}+\text{CH}_4)$ .

(d) Relative to  $k(\text{HO}+\text{CHF}_2\text{CF}_3)$ .

### Preferred Values

$k=1.4\times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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

### Reliability

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

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

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## 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  $k = 8.0 \times 10^{-19} T^2 \exp(-1170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–430 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 300 K and is derived from the three parameter equation with  $A = Ce^2 T^2$  and  $B = D + 2T$ . 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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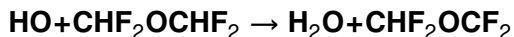
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.47 \pm 0.2) \times 10^{-14}$	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		
<i>Relative Rate Coefficients</i>			
$2.36 \times 10^{-18} T^2 \exp[-(1366 \pm 62)/T]$	298–368	Hsu and DeMore, 1995	RR (a)
$2.1 \times 10^{-15}$	298		
$2.12 \times 10^{-18} T^2 \exp[-(1313 \pm 100)/T]$	273–465	Wilson et al., 2001	RR (b)
$2.29 \times 10^{-15}$	298		

## 5 Comments

(a) HO radicals were generated from the photolysis of  $\text{H}_2\text{O}$  at 185 nm or  $\text{O}_3$  at 254 nm in the presence of  $\text{H}_2\text{O}$ . The concentrations of  $\text{CHF}_2\text{OCHF}_2$  and  $\text{CH}_3\text{CCl}_3$  were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CHF}_2\text{OCHF}_2)/k(\text{HO} + \text{CH}_3\text{CCl}_3) = (1.05 \pm 0.20) \exp[-(456 \pm 62)/T]$  is placed on an absolute basis by using the rate coefficient for

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$k(\text{HO}+\text{CH}_3\text{CCl}_3)=2.25\times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(b) HO radicals were generated from the photolysis of  $\text{H}_2\text{O}$  vapour in the reaction mixture at 185 nm. The concentrations of  $\text{CHF}_2\text{OCHF}_2$  and  $\text{CF}_3\text{CHF}_2$  were monitored by GCMS. An Arrhenius plot of the Wilson et al. (2001) data gives a rate coefficient ratio of  $k(\text{HO}+\text{CHF}_2\text{OCHF}_2)/k(\text{HO}+\text{CF}_3\text{CHF}_2)=(2.29\pm 0.06) \exp[-(193\pm 10)/T]$  over the temperature range 273–465 K. The rate coefficient ratio was placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+\text{CHF}_2\text{CF}_3)=9.24\times 10^{-19} T^2 \exp(-1120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation)

### Preferred Values

$k=2.2\times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k=1.9\times 10^{-12} \exp(-2020/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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<sub>2</sub>OCHF<sub>2</sub> 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.

5 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  $k = 2.22 \times 10^{-18} T^2 \exp(-1338/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 273–464 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 340 K with  $A = Ce^2 T^2$  and  $B = D + 2T$ .

10 Good et al. (1999) have performed experiments and ab initio calculations to determine the mechanism of CHF<sub>2</sub>OCHF<sub>2</sub> oxidation under atmospheric conditions (no kinetic data were reported). Activation barriers were calculated for various steps, and an oxidation mechanism was described.

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Wilson Jr., E. W., Sawyer, A. A., and Sawyer, H. A.: J. Phys. Chem. A., 105, 1445, 2001.

25 Zhang, Z., Saini, R. D., Kurylo, M. J., and Huie, R. E.: J. Phys. Chem., 96, 105, 9301, 1992.

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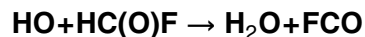
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$$\Delta H^\circ = -56.2 \text{ kJ mol}^{-1}$$

### Rate coefficient data

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

### Comments

(a) HO radicals were generated from the photolysis of  $\text{O}_3\text{-H}_2\text{-O}_2$  mixtures, and HC(O)F was formed in situ from the oxidation of  $\text{CH}_3\text{F}$ . No losses of HC(O)F were observed, leading to a rate coefficient ratio of  $k(\text{HO} + \text{HC(O)F})/k(\text{HO} + \text{CH}_3\text{F}) < 0.25$ . This upper limit to the rate coefficient ratio is placed on an absolute basis by use of  $k(\text{HO} + \text{CH}_3\text{F}) = 2.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

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

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## 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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Wallington, T. J. and Hurley, M. D.: Environ. Sci. Technol., 27, 1448, 1993.

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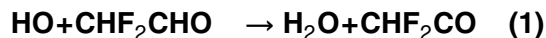
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#### IV.A1.29



$$\Delta H^\circ(1) = -110.4 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.7 \pm 0.2) \times 10^{-12}$	298 ± 2	Scollard et al., 1993	PLP-RF
<i>Relative Rate Coefficients</i>			
$(1.3 \pm 0.3) \times 10^{-12}$	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  $\text{CH}_3\text{ONO}$  (or  $\text{C}_2\text{H}_5\text{ONO}$ )- $\text{NO}-\text{CHF}_2\text{CHO}$ -toluene-air mixtures at 1 bar pressure. The concentrations of  $\text{CHF}_2\text{CHO}$  and toluene were measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CHF}_2\text{CHO})/k(\text{HO} + \text{toluene})$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO} + \text{toluene}) = 5.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Calvert et al., 2002).

(b) HO radicals were generated by the photolysis of  $\text{O}_3$  in the presence of  $\text{H}_2-\text{CHF}_2\text{CHO}$ -propane-air mixtures at 1 bar pressure. The concentrations of  $\text{CHF}_2\text{CHO}$  and propane were measured by FTIR spectroscopy. The measured

rate coefficient ratio of  $k(\text{HO}+\text{CHF}_2\text{CHO})/k(\text{HO}+\text{C}_3\text{H}_8)=1.62\pm 0.04$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+\text{C}_3\text{H}_8)=1.1\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation)

### Preferred Values

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

### Reliability

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

### Comments on Preferred Values

10 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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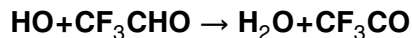
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## IV.A1.30



$$\Delta H^\circ = -107.2 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.1 \pm 0.7) \times 10^{-12}$	299±3	Dóbé et al., 1989	DF-RF
$(6.5 \pm 0.5) \times 10^{-13}$	298±2	Scollard et al. 1993	PLP-RF
<i>Relative Rate Coefficients</i>			
$(4.4 \pm 1.0) \times 10^{-13}$	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  $\text{CH}_3\text{ONO}$  (or  $\text{C}_2\text{H}_5\text{ONO}$ )- $\text{NO}$ - $\text{CF}_3\text{CHO}$ - $\text{CH}_3\text{COCH}_3$ -air mixtures at 1 bar pressure. The concentrations of  $\text{CF}_3\text{CHO}$  and  $\text{CH}_3\text{COCH}_3$  were measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CF}_3\text{CHO})/k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{CH}_3) = (2.43 \pm 0.53)$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{CH}_3) = 1.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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(b) HO radicals were generated by the photolysis of O<sub>2</sub> in the presence of H<sub>2</sub> at 1 bar pressure. FTIR was used to monitor the disappearance of reactant and reference compound. The measured rate coefficient ratio of  $k(\text{HO}+\text{CF}_3\text{CHO})/k(\text{HO}+\text{C}_2\text{H}_6)=(2.00\pm 0.13)$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO}+\text{C}_2\text{H}_6)=2.4\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation).

(c) HO radicals were generated by the photolysis of CH<sub>3</sub>ONO in the presence of NO in air at a pressure of 933 mbar. The concentrations of CF<sub>3</sub>CHO, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and reaction products were measured by FTIR spectroscopy. The measured rate coefficient ratios  $k(\text{HO}+\text{CF}_3\text{CHO})/k(\text{HO}+\text{C}_2\text{H}_2)$  and  $k(\text{HO}+\text{CF}_3\text{CHO})/k(\text{HO}+\text{C}_2\text{H}_4)$  were placed on an absolute basis by using  $k(\text{HO}+\text{C}_2\text{H}_2)=8.45\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 296 K (Sørensen et al. 2003), and  $k(\text{HO}+\text{C}_2\text{H}_4)=8.52\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 296 K (Calvert et al. 2000).

(d) Relative to C<sub>2</sub>H<sub>4</sub>.

(e) Relative to C<sub>2</sub>H<sub>4</sub>.

### Preferred Values

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

### Reliability

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

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## 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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HO+CF<sub>3</sub>C(O)OH → products

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.6 \pm 0.4) \times 10^{-13}$	315	Møgelberg et al., 1994	PR-RA
$(1.5 \pm 0.2) \times 10^{-13}$	348		
<i>Relative Rate Coefficients</i>			
$3.73 \times 10^{-19} T^2 \exp[(375 \pm 400)/T]$	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)

5 **Comments**

(a) Relative rate method. HO radicals were generated by the 254 nm photolysis of O<sub>3</sub> in the presence of water vapor in O<sub>3</sub>-H<sub>2</sub>O-CF<sub>3</sub>C(O)OH-C<sub>2</sub>H<sub>6</sub> (or C<sub>3</sub>H<sub>8</sub>)-O<sub>2</sub> mixtures. The concentrations of CF<sub>3</sub>C(O)OH and C<sub>2</sub>H<sub>6</sub> (or C<sub>3</sub>H<sub>8</sub>) were measured by FTIR spectroscopy. The measured rate coefficient ratios of  $k(\text{HO} + \text{CF}_3\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{C}_2\text{H}_6) = 0.025 \exp[(874 \pm 400)/T]$  ( $0.47 \pm 0.04$  at 298±2 K) and  $k(\text{HO} + \text{CF}_3\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{C}_3\text{H}_8) = 0.11 \pm 0.02$  at 298 K, are placed

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on an absolute basis by using rate coefficients of  $k(\text{HO} + \text{C}_2\text{H}_6) = 1.5 \times 10^{-17} T^2 \exp(-499/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation) and  $k(\text{HO} + \text{C}_3\text{H}_8) = 1.10 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC, current recommendation).

(b) Relative to  $k(\text{OH} + \text{ethane})$ .

(c) Relative to  $k(\text{OH} + \text{propane})$ .

(d) Relative rate method. HO radicals were generated by the photolysis of  $\text{O}_3$  at 254 nm in the presence of  $\text{H}_2$  in  $\text{O}_3\text{-H}_2\text{-CF}_3\text{C(O)OH-C}_2\text{H}_6\text{-O}_2$  mixtures at 740 Torr total pressure. The concentrations of  $\text{CF}_3\text{C(O)OH}$  and ethane were measured by FTIR spectroscopy. The measured rate coefficient ratio was  $k(\text{HO} + \text{CF}_3\text{C(O)OH})/k(\text{HO} + \text{C}_2\text{H}_6) = 0.59 \pm 0.04$ . If the  $(\text{CF}_3\text{C(O)OH})_2$  dimer is unreactive towards the HO radical, then the rate coefficient ratio corrected for dimer formation is  $0.84 \pm 0.06$ . An average value of  $k(\text{HO} + \text{CF}_3\text{C(O)OH})/k(\text{HO} + \text{C}_2\text{H}_6) = 0.72 \pm 0.18$  was preferred and is placed on an absolute basis by using a rate coefficient of  $k(\text{HO} + \text{C}_2\text{H}_6) = 2.43 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K (IUPAC, current recommendation).

(e) Relative rate method. HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO}$  in the presence of NO in air.  $\text{CH}_3\text{ONO-NO-CF}_3\text{C(O)OH}$ -reference compound-air mixtures at 700 Torr total pressure were photolysed by UV lamps. Reference compounds were  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$ . The concentrations of  $\text{CF}_3\text{C(O)OH}$ ,  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  were measured by FTIR spectroscopy. The measured rate constant ratios of  $k(\text{HO} + \text{CF}_3\text{C(O)OH})/k(\text{HO} + \text{C}_2\text{H}_2) = 0.103 \pm 0.017$  and  $k(\text{HO} + \text{CF}_3\text{C(O)OH})/k(\text{HO} + \text{C}_2\text{H}_4) = 0.0116 \pm 0.0012$  are placed on an absolute basis by using rate coefficients of  $k(\text{HO} + \text{C}_2\text{H}_2) = 8.45 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Sørensen et al., 2003) and  $k(\text{HO} + \text{C}_2\text{H}_4) = 8.66 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Calvert et al. 2000), both at 296 K and 700 Torr of air.

(f) Relative to  $k(\text{HO}+\text{acetylene})$ .

(g) Relative to  $k(\text{HO}+\text{ethene})$ .

### Preferred Values

$k = 1.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , 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  $\text{H}_2\text{O} + \text{CF}_3\text{CO}_2$  (see the data sheets on the HO radical reactions with  $\text{HC}(\text{O})\text{OH}$  and  $\text{CH}_3\text{C}(\text{O})\text{OH}$ ).

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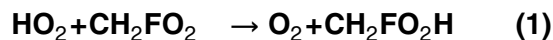
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## IV.A1.32



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

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

### 5 Comments

(a)  $\text{HO}_2$  and  $\text{CH}_2\text{FO}_2$  radicals were generated from the steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{F}$ - $\text{H}_2$ -air mixtures at total pressures of 400–933 mbar. The branching ratios were derived from FTIR analysis of  $\text{CH}_2\text{FO}_2\text{H}$  and  $\text{HCOF}$ , which accounted for  $100 \pm 13\%$  of the loss of  $\text{CH}_3\text{F}$ .

### 10 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.

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## 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<sub>2</sub> reactions with substituted peroxy radicals, for example, with HOCH<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> radicals.

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## IV.A1.33



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Branching Ratios</i>			
$\leq 2 \times 10^{-12}$	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)

### 5 Comments

(a) Flash photolysis of  $\text{H}_2\text{O}_2$  in the presence of  $\text{CF}_3\text{CH}_2\text{F-O}_2\text{-N}_2$  mixtures at a total pressure of 1013 mbar. Primary investigation of  $\text{CF}_3\text{CHFO}_2$  radical kinetics, with  $\text{CF}_3\text{O}_2$  radicals generated from the decomposition of product  $\text{CF}_3\text{CHFO}$  radicals. Decays in transient absorption signals (with contributions from  $\text{CF}_3\text{CHFO}_2$ ,  $\text{HO}_2$  and  $\text{CF}_3\text{O}_2$ ) 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  $\text{CF}_3\text{O}_2 + \text{HO}_2$  was occurring appreciably under the experimental conditions.

(b) Pulse radiolysis study of  $\text{CHF}_3\text{-H}_2\text{-O}_2\text{-SF}_6$  mixtures at a total pressure of 1013 mbar.  $\text{CF}_3\text{O}_2$  and  $\text{HO}_2$  radicals were monitored by UV absorption spectroscopy at 230 nm. Decays in transient absorption signals (with contributions

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from HO<sub>2</sub> and CF<sub>3</sub>O<sub>2</sub>) 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<sub>3</sub>O<sub>2</sub> and HO<sub>2</sub> radicals were produced by the F+CHF<sub>3</sub> and F+CH<sub>3</sub>OH reactions, with subsequent addition of O<sub>2</sub>. Both CF<sub>3</sub>O<sub>2</sub> and HO<sub>2</sub> were monitored by titration to NO<sub>2</sub> following reaction with excess NO, with detection of NO<sub>2</sub> 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  $<(1-3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

## 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<sub>2</sub> with CF<sub>3</sub>O<sub>2</sub>, 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.

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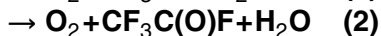
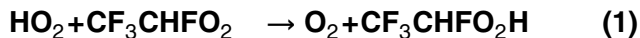
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#### IV.A1.34



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.8 \times 10^{-13} \exp[(910 \pm 220)/T]$	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)
<i>Branching Ratios</i>			
$k_1/k > 0.95$	296	Maricq et al., 1994	UVP-FTIR (d)
$k_2/k < 0.05$	296		

#### 5 Comments

(a) Flash photolysis time-resolved UV absorption study of  $\text{F}_2\text{-CF}_3\text{CH}_2\text{F-H}_2\text{-O}_2\text{-N}_2$  mixtures. The rate coefficients were obtained from a fit of the decay curves for  $\text{CF}_3\text{CHFO}_2$ ,  $\text{HO}_2$ ,  $\text{CF}_3\text{O}_2$  and  $\text{ROOH}$ , based on a mechanism of 14 reactions.

(b) Flash photolysis of  $\text{H}_2\text{O}_2$  in the presence of  $\text{CF}_3\text{CH}_2\text{F-O}_2\text{-N}_2$  mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contribu-

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tions from  $\text{CF}_3\text{CHFO}_2$ ,  $\text{HO}_2$  and  $\text{CF}_3\text{O}_2$ ) were recorded in the wavelength range 220 nm to 240 nm.  $k$  derived from simulations of the decay traces using a 15 reaction mechanism.

5 (c) Pulse radiolysis study of  $\text{CF}_3\text{CH}_2\text{F-H}_2\text{-O}_2\text{-SF}_6$  mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from  $\text{CF}_3\text{CHFO}_2$ ,  $\text{HO}_2$  and  $\text{CF}_3\text{O}_2$ ) 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.

10 (d) Steady-state photolysis of  $\text{Cl}_2\text{-CF}_3\text{CH}_2\text{F-H}_2\text{-O}_2\text{-N}_2$  mixtures with FTIR analysis of the products  $\text{HC(O)F}$ ,  $\text{CF}_3\text{C(O)F}$ ,  $\text{C(O)F}_2$  and  $\text{CF}_3\text{O}_3\text{CF}_3$ . The branching ratio,  $k_2/k$ , cited above was based on measurements of  $\text{CF}_3\text{COF}$ , and the value of  $k_1/k$  was inferred.

### Preferred Values

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

15  $k = 2.0 \times 10^{-13} \exp(910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 210–365 K.

$k_1/k = 1.0$  at 298.

### Reliability

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

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

20  $\Delta (k_1/k) = \begin{matrix} +0.0 \\ -0.1 \end{matrix}$  at 298 K.

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  $k$

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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<sub>2</sub> with C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>. This confirms a deactivating influence of  $\alpha$ -F and  $\alpha$ -CF<sub>3</sub> groups, observed for the reactions of a number of halogenated peroxy radicals with HO<sub>2</sub>.

## 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.

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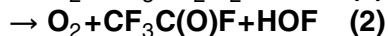
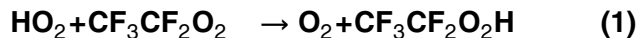
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## IV.A1.35



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

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

### 5 Comments

(a) Flash photolysis of  $\text{H}_2\text{O}_2$  in the presence of  $\text{CF}_3\text{CHF}_2\text{-O}_2\text{-N}_2$  mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from  $\text{CF}_3\text{CF}_2\text{O}_2$ ,  $\text{HO}_2$  and  $\text{CF}_3\text{O}_2$ ) 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

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

### Reliability

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

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## 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  $\text{HO}_2$  with  $\text{C}_2\text{H}_5\text{O}_2$ . This confirms a deactivating influence of  $\alpha$ -F and  $\alpha$ - $\text{CF}_3$  groups, observed for the reactions of a number of halogenated peroxy radicals with  $\text{HO}_2$ .

## References

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

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**FO<sub>2</sub>+CO → products****Rate coefficient data**

<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
<5.1 × 10 <sup>-16</sup>	298	Sehested et al., 1994	PR-UVA (a)

5 **Comments**

(a) Pulse radiolysis of CO-O<sub>2</sub>-SF<sub>6</sub> mixtures in a high pressure cell at 18 bar SF<sub>6</sub>. The decay of FO<sub>2</sub> radicals was monitored in absorption at 220 nm.

**Preferred Values**

< 6 × 10<sup>-16</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K.

10 **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.

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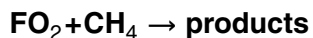
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Sehested, J., Sehested, K., Nielsen, O. J., and Wallington, T. J.: J. Phys. Chem., 98, 6731, 1994.

### 5 IV.A1.37



## Rate coefficient data

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

## Comments

- 10 (a) Pulse radiolysis/UV absorption spectroscopy technique. Pulse radiolysis of  $\text{CH}_4\text{-O}_2\text{-SF}_6$  mixtures in a high pressure cell at 18 bar  $\text{SF}_6$ . The decay of  $\text{FO}_2$  radicals was monitored in absorption at 220 nm.

## Preferred Values

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

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## 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.

### 5 References

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

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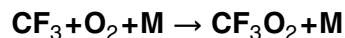
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$$\Delta H^\circ(1) = -148 \text{ kJ mol}^{-1}$$

### Low-pressure rate coefficients

#### Rate coefficient data

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

#### Comments

- (a) Microwave discharge-flow system coupled to quadrupole MS.  $\text{CF}_3$  radicals monitored by MS. Measurements over the range 0.7–11 mbar, extrapolated with  $F_c \approx 0.4$  and  $k_\infty \approx 8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (b) Pulsed laser photolysis-MS study over the range 0.3–16 mbar. Extrapolation with  $F_c \approx 0.6$  and  $k_\infty \approx 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (c) Pulsed laser photolysis-IR chemiluminescence study of  $\text{CF}_3\text{I}$  in the presence of  $\text{NO}_2$  and  $\text{O}_2$ , using IR emission from the reaction  $\text{CF}_3 + \text{NO}_2$  for detection. Pressure range 2.7–150 mbar. Extrapolation with  $F_c \approx 0.6$  and  $k_\infty \approx 2.55 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , using data up to 800 mbar from relative rate measurements by Kaiser et al. (1995).

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## Preferred Values

$k_0 = 2.2 \times 10^{-29} (T/300)^{-4.7} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230–380 K.

## Reliability

- 5  $\Delta \log k_0 = \pm 0.1$  at 298 K.  
 $\Delta n = \pm 1.5$ .

## Comments on Preferred Values

10 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  $k_\infty$  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

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

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## Comments

(a) Pulse radiolysis of  $\text{CF}_3\text{Cl}$ .  $\text{CF}_3\text{O}_2$  detected by UV absorption spectroscopy near 260 nm. Measurements in 920 mbar of Ar.

(b) UV irradiation of  $\text{CF}_3\text{I}-\text{CH}_4-\text{Cl}_2-\text{N}_2-\text{O}_2$  mixtures and observation of loss of  $\text{CF}_3$  and  $\text{CH}_4$ . Measurement of the ratio  $k(\text{CF}_3+\text{O}_2)/k(\text{CF}_3+\text{Cl}_2)$  as a function of the pressure and calibration of this ratio at low pressures against  $k_0(\text{CF}_3+\text{O}_2)$  from Caralp et al. (1986). Inspection of the spectra recorded by Cooper et al. (1980) and comparison with more recently detected spectra of  $\text{CF}_3\text{O}_2$  indicates that the rate of  $\text{CF}_3+\text{O}_2$  was not observed by Cooper et al. (1980).

## Preferred Values

$k_\infty = 4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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  $k_\infty$ , the results from the relative rate measurements from Kaiser et al. (1995) are preferred. They are similar as values for  $k_\infty$  for  $\text{CCl}_3+\text{O}_2$  from Luther et al. (2001) for which  $n = -1.4$  was measured. Using an estimated  $F_o = 0.39$  independent of the temperature, all results (except those from Cooper et al. (1980)) are consistently represented and the remaining uncertainty of  $k_\infty$  does not impact on  $k_0$ .

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Breheeny, 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.

5 Cooper, R., Cumming, J. B., Gordon, S., and Mulac, W. A.: Rad. Phys. Chem., 16, 169, 1980.

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.

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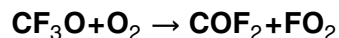
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## IV.A1.39



$$\Delta H^\circ(1) = 47.0 \text{ kJ mol}^{-1}$$

### Rate coefficient data

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

### Comments

(a)  $\text{CF}_3\text{O}$  radicals were generated by photolysis of  $\text{CF}_3\text{OOCF}_3$  at 193 nm.

### Preferred Values

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

$k < 1 \times 10^{-10} \exp(-5600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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  $k(298 \text{ K})$ . This procedure using the high temperature limit yields a room temperature

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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  $\text{CF}_3\text{O}$  with NO found no evidence for the reaction of  $\text{CF}_3\text{O}$  with  $\text{O}_2$  in 1 bar of air at room temperature.

## 5 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.

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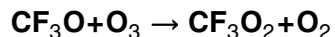
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#### IV.A1.40



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

#### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<1 \times 10^{-13}$	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	Mellor and Moortgat, 1995	(f)
$(1.3 \pm 0.5) \times 10^{-14}$	298	Bourbon et al., 1996	FT/LIF (g)
<i>Relative Rate Coefficients</i>			
$<3 \times 10^{-14}$	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  $\text{CHF}_3\text{-O}_2\text{-O}_3\text{-SF}_6$  mixtures. Upper limit for  $k$  derived from simulations of ozone absorption transients at 254 nm and 276 nm in the presence of  $\text{CF}_3\text{O}$  and  $\text{CF}_3\text{O}_2$  radicals.

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(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  $k(CF_3O+CH_4)=2.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC, current recommendation).

### Preferred Values

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

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

### Reliability

$\Delta \log k = \pm 1$  at 298 K.

$\Delta (E/R) = \pm 600 \text{ K}$ .

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## 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  $\text{CF}_3\text{O}$  reactions, and the value of  $E/R$  fitted to the preferred room temperature value.

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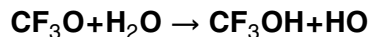
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#### IV.A1.41



$$\Delta H^\circ(1) = 43.4 \text{ kJ mol}^{-1}$$

#### Rate coefficient data

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

#### Comments

(a) Pulsed laser photolysis/pulsed laser induced fluorescence technique.  $\text{CF}_3\text{O}$  radicals were generated by photolysis of  $\text{CF}_3\text{OOCF}_3$  at 193 nm.

(b) Long path FTIR-based study.  $\text{CF}_3\text{O}$  radicals generated by chlorine-initiated oxidation of  $\text{CF}_3\text{CFH}_2$  (HFC-134a) in photolytic mixture of  $\text{Cl}_2\text{-CF}_3\text{CFH}_2\text{-H}_2\text{O}$  in 1 bar air. Reaction rate studied in competition with the rate of  $\text{CF}_3\text{O} + \text{CF}_3\text{CFH}_2$ .

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## Preferred Values

$k < 2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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

## Comments on Preferred Values

- 5 The *A*-factor is estimated by analogy with similar reactions of CF<sub>3</sub>O 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.

## 10 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.

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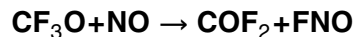
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$$\Delta H^\circ = -135 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.2 \pm 2.7) \times 10^{-11}$	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	FT/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/LAS (f)

### Comments

- (a) Radicals generated by pulse radiolysis of  $\text{CHF}_3\text{-O}_2\text{-NO-SF}_6$  mixtures. Value of  $k$  derived from simulations of FNO absorption transients at 310.5 nm.
- (b)  $\text{CF}_3\text{O}$  radicals were generated by photolysis of  $\text{CF}_3\text{OOCF}_3$  at 193 nm.
- (c) Flow tube reactor/chemical ionization mass spectrometer technique.  $\text{CF}_3\text{O}$  radicals were generated by pyrolysis of  $\text{CF}_3\text{OOCF}_3$ . A low value of  $k$  from the same

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laboratory reported earlier by Bevilacqua et al. (1993) is superseded by these results.

- (d)  $\text{CF}_3\text{O}$  radicals were generated by DF technique in  $\text{F}/\text{CF}_3\text{H}/\text{O}_2/\text{NO}$  system.
- (e)  $k$  obtained by modeling NO time dependence during secondary reactions in  $\text{CF}_3\text{O}_2 + \text{NO}$  reaction.
- (f)  $\text{CF}_3\text{O}$  radicals were generated by photolysis of  $\text{CF}_3\text{OOCF}_3$  at 193 nm. Time resolved formation of  $\text{COF}_2$  using tunable diode laser absorption near  $1950\text{ cm}^{-1}$ . FNO identified as major co-product with  $\text{COF}_2$ .

### Preferred Values

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

### Reliability

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

### 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)

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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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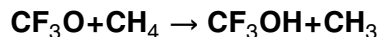
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## IV.A1.43



$$\Delta H^\circ(1) = -16.9 \text{ kJ mol}^{-1}$$

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.2 \pm 0.2) \times 10^{-14}$	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	FT/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	FT/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)
$2.5 \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$< 5 \times 10^{-15}$	297	Chen et al., 1992	(f)
$(1.2 \pm 0.1) \times 10^{-14}$	298	Kelly et al., 1993	(g)

## Comments

(a)  $\text{CF}_3\text{O}$  radicals were generated by photolysis of  $\text{CF}_3\text{OF}$  at 248 nm.

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(b)  $\text{CF}_3\text{O}$  radicals were generated by photolysis of  $\text{CF}_3\text{OOCF}_3$  at 193 nm.

(c)  $\text{CF}_3\text{O}$  radicals were generated by pyrolysis of  $\text{CF}_3\text{OOCF}_3$ .

(d)  $\text{CF}_3\text{O}$  radicals were generated by the pyrolysis of  $\text{CF}_3\text{OOCF}_3$ .

(e)  $\text{CF}_3\text{O}$  radicals were generated by photolysis of  $\text{CF}_3\text{OF}$  at 248 nm.

5 (f) Long path FTIR-based product study of visible photolysis of  $\text{CF}_3\text{NO-NO-CH}_4$  mixtures in 700 torr air. Searched for  $\text{CH}_2\text{O}$  product from oxidation of  $\text{CH}_4$  initiated by reaction of  $\text{CF}_3\text{O}$  radicals with  $\text{CH}_4$ . Upper limit of  $k$  given in table is derived from the measured ratio  $k/k(\text{CF}_3\text{O+NO}) < 10^{-4}$  and the value of  $k(\text{CF}_3\text{O+NO})$  given in this evaluation.

10 (g) Long-path FTIR-based study.  $\text{CF}_3\text{O}$  radicals were generated by photolysis of  $\text{CF}_3\text{OOCF}_3$ . 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  $k/k(\text{CF}_3\text{O+C}_2\text{H}_6)=0.010\pm 0.001$  and the value of  $k(\text{CF}_3\text{O+C}_2\text{H}_6)$  (IUPAC, current evaluation).

### 15 Preferred Values

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

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

### Reliability

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

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

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## 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  $k/k(\text{CF}_3\text{O}+\text{C}_2\text{H}_6)=0.0152\pm 0.0023$  at 296 K in good agreement with the recommended rate coefficients. Jensen et al. (1994) detected the product  $\text{CF}_3\text{OH}$  by chemical ionization mass spectrometer (CIMS) and observed its formation to correlate with the loss of the  $\text{CF}_3\text{O}$  reactant. The  $\text{CF}_3\text{OH}$  product of this reaction was also observed by Bevilacqua et al. (1993) and also by Bednarek et al. (1994), who used FTIR spectroscopy to show that  $\text{CF}_3\text{OH}$  is converted slowly to  $\text{C}(\text{O})\text{F}_2$ .

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5 Wallington, T. J. and Ball, J. C.: J. Phys. Chem., 99, 3201, 1995.

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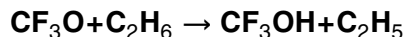
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## IV.A1.44



$$\Delta H^\circ(1) = -32.2 \text{ kJ mol}^{-1}$$

## Rate coefficient data

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

## Comments

- (a) Laser photolysis/laser induced fluorescence technique.  $\text{CF}_3\text{O}$  radicals were generated by the photolysis of  $\text{CF}_3\text{OF}$  at 248 nm.
- (b) Pulsed laser photolysis/pulsed laser induced fluorescence technique.  $\text{CF}_3\text{O}$  radicals were generated by the photolysis of  $\text{CF}_3\text{OOCF}_3$  at 193 nm.
- (c) Fast flow tube (~1.3 mb pressure)/laser induced fluorescence.  $\text{CF}_3\text{O}$  radicals were generated by the pyrolysis of  $\text{CF}_3\text{OOCF}_3$  at 193 nm.

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(d) Long path FTIR-based product study of visible photolysis of  $\text{CF}_3\text{NO}-\text{NO}-\text{C}_2\text{H}_6$  mixtures in 700 Torr air. The upper limit of  $k$  given in table is derived from measured ratio  $k/k(\text{CF}_3\text{O}+\text{NO})=0.02\pm 0.006$  and the value of  $k(\text{CF}_3\text{O}+\text{NO})$  (IUPAC, current recommendation).

## 5 Preferred Values

$k=1.3\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

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

## Reliability

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

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

## 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  $\text{CF}_3\text{O}$  reaction with a number of hydrocarbons relative to the rate of the reaction of  $\text{CF}_3\text{O}$  with  $\text{C}_2\text{H}_6$ . They reported  $k(\text{CF}_3\text{O}+\text{CH}_4)/k=0.010\pm 0.001$  at 298 K and 1 bar pressure (Kelly et al., 1993). This

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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  $k(\text{CF}_3\text{O}+\text{CH}_4)/k=0.0152\pm 0.0023$  at 296 K in good agreement with the recommended rate coefficients.

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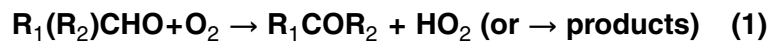
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#### IV.A1.45-54



R=alkyl, halogenated alkyl, H or halogen atom

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## Rate coefficient data

Reaction Number	Reactions	$k_1/k_2^{-1}/\text{cm}^2 \text{ molecule}^{-1}$	Temp./K	Reference	Comments
IV.A1.45	$\text{CH}_2\text{FO} + \text{O}_2 \rightarrow \text{HCOF} + \text{HO}_2$	(1) $k_1[\text{O}_2] \gg k_2$ (933 mbar, air)	298	Edney and Driscoll, 1992	(a)
IV.A1.46	$\text{CH}_2\text{FO} + \text{M} \rightarrow \text{HCOF} + \text{H} + \text{M}$	(2) $k_1[\text{O}_2] \gg k_2$ (986 mbar, air)	298	Tuazon and Atkinson, 1993a	(a)
IV.A1.47	$\text{CH}_3\text{CF}_2\text{O} + \text{O}_2 \rightarrow \text{products}$	(1) $k_1[\text{O}_2] \ll k_2$ (933 mbar, air)	298	Edney and Driscoll, 1992	(b)
IV.A1.48	$\text{CH}_3\text{CF}_2\text{O} + \text{M} \rightarrow \text{CH}_3 + \text{COF}_2 + \text{M}$	(2) $k_1[\text{O}_2] \ll k_2$ (986 mbar, air)	298	Tuazon and Atkinson, 1993a	(c)
IV.A1.49	$\text{CH}_2\text{FCHFO} + \text{O}_2 \rightarrow \text{CH}_2\text{FCOF} + \text{HO}_2$	(1) $k_1[\text{O}_2] \ll k_2$ (933 mbar, air)	296	Wallington et al., 1994	(d)
IV.A1.50	$\text{CH}_2\text{FCHFO} + \text{M} \rightarrow \text{CH}_2\text{F} + \text{HCOF} + \text{M}$	(2)			
IV.A1.51	$\text{CF}_3\text{CHFO} + \text{O}_2 \rightarrow \text{CF}_3\text{COF} + \text{HO}_2$	(1) $1.58 \times 10^{-25} \exp(3600/T)$	296	Wallington et al., 1992	(e)
IV.A1.52	$\text{CF}_3\text{CHFO} + \text{M} \rightarrow \text{CF}_3 + \text{HCOF}$	(2) $2.8 \times 10^{-20}$ (2 bar)	298		
		$3.2 \times 10^{-25} \exp(3510/T)$	273–320	Tuazon and Atkinson, 1993b	(f)
		$4.5 \times 10^{-20}$ (986 mbar)	298		
		$k_2 = 3.7 \times 10^7 \exp(-2200/T) \text{ s}^{-1}$	211–372	Maricq and Szente, 1992	(g)
		$k_2 = 2.3 \times 10^4 \text{ s}^{-1}$ (307 mbar)	298		
		$1.18 \times 10^{-24} \exp(2860/T)$	235–318	Rattigan et al., 1994	(h)
		$1.7 \times 10^{-20}$ (1 bar)	298		
		$1.5 \times 10^{-19}$ (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)

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Reaction Number	Reactions	$k_1/k_2^{-1}/\text{cm}^2 \text{ molecule}^{-1}$	Temp./K	Reference	Comments
IV.A1.53	$\text{CF}_3\text{CF}_2\text{O} + \text{O}_2 \rightarrow \text{products}$	(1) $k_1[\text{O}_2] \ll k_2$ (933 mbar, air)	298	Edney and Driscoll, 1992	(l)
IV.A1.54	$\text{CF}_3\text{CF}_2\text{O} + \text{M} \rightarrow \text{CF}_3 + \text{CF}_2\text{O} + \text{M}$	(2) $k_1[\text{O}_2] \ll k_2$ (986 mbar, air)		Tuazon and Atkinson, 1993a	(m)

## Comments

- (a) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{F}$ -air mixtures (1 atm) with FTIR absorption spectroscopic analysis: a 100% yield of  $\text{HCOF}$  was observed, consistent with  $k_1[\text{O}_2] \gg k_2$ .
- (b) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{CHF}_2$ -air mixtures (1 atm) with FTIR absorption spectroscopic analysis: a  $100 \pm 5\%$  yield of  $\text{COF}_2$  was observed, consistent with  $k_1[\text{O}_2] \ll k_2$ .
- (c) Similar experiments to those of Comment (b); a  $92.2 \pm 1.2\%$  yield of  $\text{COF}_2$ , plus other unidentified products, was observed, consistent with  $k_1[\text{O}_2] \ll k_2$ .
- (d) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_2\text{FCH}_2\text{F}$ -air mixtures (933 mbar) with FTIR analysis: a  $91 \pm 10\%$  yield of  $\text{HCOF}$  was observed, consistent with  $k_1[\text{O}_2] \ll k_2$ .
- (e) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CF}_3\text{CFH}_2$ - $\text{O}_2$ - $\text{N}_2$  mixtures at total pressures of 2 atm with FTIR analysis of products  $\text{CF}_3\text{COF}$  and  $\text{HCOF}$ . 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.

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- 5 (g) Flash-photolysis time-resolved UV absorption spectroscopic study of  $\text{CF}_3\text{CHFO}_2$  radicals from  $\text{F}_2\text{-CF}_3\text{CH}_2\text{F-O}_2\text{-N}_2$  mixtures,  $k_1$  obtained from a fit of  $\text{CF}_3\text{O}_2$  formation profiles, produced from reaction (1) followed by  $\text{CF}_3 + \text{O}_2 + \text{M}$ . Experiments were carried out at a total pressure of 306 mbar, well below the high-pressure limit.
- (h)  $\text{Cl}_2$ -initiated photooxidation of  $\text{CF}_3\text{CH}_2\text{F}$  at 1 atm pressure, with dual-beam diode-array UV spectroscopic determination of  $\text{CF}_3\text{COF}$  and  $\text{HCOF}$  products.
- 10 (i) Direct time-resolved experiment using laser pulsed photolysis-laser long path absorption;  $\text{CF}_3\text{CFHO}$  produced by  $\text{CF}_3\text{CFHO}_2 + \text{NO}$  reaction and kinetics of thermal decomposition reaction determined at  $p=50$  mbar and 295 K. The relative 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.
- 15 (j) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CF}_3\text{CFH}_2\text{-O}_2\text{-N}_2$  mixtures at total pressures of 55–800 mbar with FTIR analysis of products  $\text{CF}_3\text{COF}$  and  $\text{HCOF}$ . Experiments also carried out with  $\text{NO}$  present so that  $\text{CF}_3\text{CFHO}$  was produced by  $\text{CF}_3\text{CFHO}_2 + \text{NO}$  reaction, as opposed to the self reaction of  $\text{CF}_3\text{CFHO}_2$ . 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  $\text{NO}$  experiments. This was ascribed to the production of vibrationally hot  $\text{CF}_3\text{CFHO}$  radicals which decompose promptly to  $\text{CF}_3 + \text{HCFO}$ , in the more exothermic source reaction.
- 20 (k) Steady-state photolysis of  $\text{F}_2$  in the presence of  $\text{CF}_3\text{CFH}_2\text{-O}_2\text{-N}_2$  mixtures ( $p=910$  mbar) with FTIR absorption spectroscopic analysis.
- 25 (l) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CF}_3\text{CHF}_2\text{-air}$  mixtures (1 atm) with FTIR absorption spectroscopic analysis; a  $109 \pm 5\%$  yield of  $\text{C(O)F}_2$  was observed, consistent with  $k_1[\text{O}_2] \ll k_2$ .

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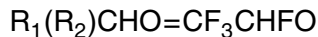
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(m) Similar experiments to those in Comment (l) at a total pressure of 986 mbar; a ~ 100% yield of C(O)F<sub>2</sub> was observed consistent with  $k_1[\text{O}_2] \ll k_2$ .

### Preferred Values

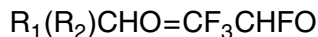


5  $k_1/k_2=2.7 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1}$  at 298 K and 1 atm pressure.

$k_1/k_2=2.1 \times 10^{-25} \exp(3625/T) (1 \text{ bar}) \text{ cm}^3 \text{ molecule}^{-1}$  over the temperature range 260–355 K.

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

### 10 *Comments on Preferred Values*



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).

15 The data were corrected for a small pressure dependence measured by Wallington et al. (1996) at 298 K and the expression refers to reactions of the thermalised CF<sub>3</sub>CHFO radicals. This study also revealed that energy rich CF<sub>3</sub>CHFO radicals were formed when the radical was produced from the CF<sub>3</sub>CHFO<sub>2</sub>+NO reaction, leading to formation of HC(O)F by prompt decomposition at atmospheric temperatures, reducing  
20 the relative rate of O<sub>2</sub> reaction by a factor of 1.8–4.0. Several theoretical studies have investigated the decomposition of CF<sub>3</sub>CHFO radicals and have confirmed that this interpretation is realistic. (Schneider et al., 1998; Somnitz and Zellner, 2001).

R<sub>1</sub>(R<sub>2</sub>)CHO=other radicals in the above table.

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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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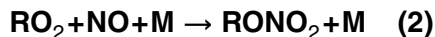
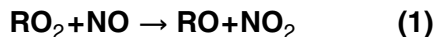
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(R=CH<sub>2</sub>F, CHF<sub>2</sub>, CF<sub>3</sub>, CH<sub>2</sub>FCHF, CHF<sub>2</sub>CF<sub>2</sub>, CF<sub>3</sub>CHF, CF<sub>3</sub>CF<sub>2</sub>)

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

Reaction Number	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>				
IV.A1.55	R=CH <sub>2</sub> F (1.25±0.13)×10 <sup>-11</sup>	295	Sehested et al., 1993	PR-AS (a)
IV.A1.56	R=CHF <sub>2</sub> (1.26±0.16)×10 <sup>-11</sup>	295	Sehested et al., 1993	PR-AS (a)
IV.A1.57	R=CF <sub>3</sub> (1.78±0.36)×10 <sup>-11</sup>	295	Plumb and Ryan, 1982	DF-MS (b)
	1.45×10 <sup>-11</sup> (T/298) <sup>-(1.2±0.2)</sup>	230–430	Dognon et al., 1985	PLP-MS (c)
	(1.45±0.20)×10 <sup>-11</sup>	298		
	(1.53±0.30)×10 <sup>-11</sup>	290	Peeters et al., 1992	DF-MS (d)
	(1.68±0.26)×10 <sup>-11</sup>	295	Sehested and Nielsen, 1993	PR-AS (a)
	(1.53±0.20)×10 <sup>-11</sup>	297	Bevilacqua et al., 1993	F-CIMS (e)
	(1.57±0.38)×10 <sup>-11</sup>	298	Turnipseed et al., 1994	PLP-LIF (f)
	(1.57±0.31)×10 <sup>-11</sup>	293	Bhatnagar and Carr, 1994	FP-MS (g)

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Reaction Number	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>				
IV.A1.58	$(1.76 \pm 0.35) \times 10^{-11}$	298	Bourbon et al., 1996	DF-LIF (h)
	$(1.6 \pm 0.3) \times 10^{-11}$	298	Louis et al., 1999	DF-MS (i)
	R=CH <sub>2</sub> FCHF			
	$> 8.7 \times 10^{-12}$	296	Wallington et al., 1994	PR-AS (a)
IV.A1.59	R=CHF <sub>2</sub> CF <sub>2</sub>			
	$> (9.7 \pm 1.3) \times 10^{-12}$	295	Sehested et al., 1993	PR-AS (a)
IV.A1.60	R=CF <sub>3</sub> CHF			
	$(1.28 \pm 0.36) \times 10^{-11}$	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 <sub>3</sub> CF <sub>2</sub>			
	$> (1.07 \pm 0.15) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
<i>Branching Ratios</i>				
IV.A1.57	R=CF <sub>3</sub>			
	$k_2/k = (0.0167 \pm 0.0027)$	295	Nishida et al., 2004	P-FITR (k)

## Comments

- (a)  $k$  determined from  $+d[\text{NO}_2]/dt$  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.

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- (d) Fast-flow system with molecular beam sampling MS at a total pressure of 2.7 mbar.  $k$  was derived from decay of  $\text{CF}_3\text{O}_2$  and appearance of  $\text{NO}_2$ .
- (e)  $k$  determined from decay of  $\text{CF}_3\text{O}_2$  in the presence of NO; pressure range 1.1–2.7 mbar.
- 5 (f) Photolysis of  $\text{CF}_3\text{Br}$  in the presence of  $\text{O}_2$  and NO at 93 mbar total pressure.  $k$  was obtained by fitting the measured  $\text{CF}_3\text{O}$  radical temporal profile, with formation through  $\text{CF}_3\text{O}_2 + \text{NO}$  and loss through  $\text{CF}_3\text{O} + \text{NO}$ .
- (g) Photolysis of  $(\text{CF}_3\text{CO})_2\text{O}$  in the presence of  $\text{O}_2$ ,  $\text{N}_2$  and NO at 2.7–40 mbar total pressure.  $k$  obtained from the kinetics of  $\text{CF}_3\text{O}_2$  removal and  $\text{CF}_3\text{O}$  formation.  $k$  was independent of pressure in the studied range.
- 10 (h)  $\text{CF}_3\text{O}_2$  generated from  $\text{F} + \text{CHF}_3$  reaction, with  $k$  determined from the formation kinetics of  $\text{CF}_3\text{O}$  when NO added; pressure range 1.1–4.0 mbar.
- (i)  $\text{CF}_3\text{O}_2$  generated from  $\text{F} + \text{CHF}_3$  reaction, with  $k$  determined from the removal kinetics of  $\text{CF}_3\text{O}_2$  when NO added; pressure range 0.9–4.0 mbar.
- 15 (j) Photolysis of  $\text{Cl}_2$  in the presence of  $\text{CF}_3\text{CH}_2\text{F}$ ,  $\text{O}_2$ ,  $\text{N}_2$  and NO at 16–33 mbar total pressure.  $k$  was obtained from the formation kinetics of  $\text{NO}_2$ .  $k$  was independent of pressure in the studied range.
- (k)  $\text{CF}_3\text{O}_2$  generated from the UV photolysis of  $\text{CF}_3\text{N}_2\text{CF}_3$  in excess NO,  $\text{N}_2$  and  $\text{O}_2$  at 930 mbar. Branching ratio determined from the relative yields of  $\text{CF}_3\text{ONO}_2$  and  $\text{COF}_2$ .
- 20

### Preferred Values

$\text{R} = \text{CH}_2\text{F}$

$k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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

R=CHF<sub>2</sub>

$k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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

R=CF<sub>3</sub>

$k = 1.6 \times 10^{-11} (T/298)^{-1.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230–430 K.

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

$\Delta n = \pm 0.5$ .

R=CH<sub>2</sub>FCHF

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

15

R=CHF<sub>2</sub>CF<sub>2</sub>

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

R=CF<sub>3</sub>CHF

20  $k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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

R=CF<sub>3</sub>CF<sub>2</sub>

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

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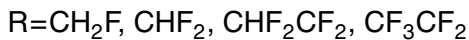
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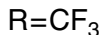
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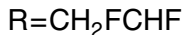
## Comments on Preferred Values



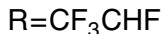
The preferred values are the rounded-off rate coefficients determined by Sehested et al. (1993).



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).



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



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,  $\text{CH}_3\text{O}_2$  and  $\text{C}_2\text{H}_5\text{O}_2$ , indicates that the presence of a  $\alpha$ -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  $\alpha$ -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

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al. (1985) measured quantum yields for NO<sub>2</sub> greater than unity for all the RO<sub>2</sub> radicals studied; suggesting that the RO<sub>2</sub>+NO reactions mainly form RO and NO<sub>2</sub>, with additional NO<sub>2</sub> being produced from secondary chemistry. Recently, Nishida et al. (2004) have observed formation of a small yield 1.7±0.3% of CF<sub>3</sub>ONO<sub>2</sub> from the reaction of CF<sub>3</sub>O<sub>2</sub> with NO, confirming the existence of channel (2) at 930 mbar pressure. This suggests that the reactions of the C<sub>1</sub> and C<sub>2</sub> halogenated RO<sub>2</sub> radicals will generally have minor channels forming RONO<sub>2</sub>, but additional studies are required to confirm this.

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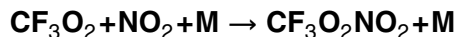
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$$\Delta H^\circ = -105 \text{ kJ mol}^{-1}$$

### Low-pressure rate coefficients

#### 5 Rate coefficient data

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

#### Comments

(a) Pulsed laser photolysis-MS study in 1–10 Torr  $\text{O}_2$ . Extrapolation with  $F_c = \exp(-T/416)$ , i.e.,  $F_c = 0.49$  at 298 K, and  $k_\infty = 8.9 \times 10^{-12} (T/298)^{-0.72} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from RRKM model.

(b) From measurements of the reverse dissociation of  $\text{CF}_3\text{O}_2\text{NO}_2$ . Equilibrium constants  $K_c = 3.80 \times 10^{27} \exp(-12140/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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  $\text{N}_2$  and  $\text{O}_2$ . Extrapolation with  $F_c = 0.31$  and  $k_\infty = 7.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

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## Preferred Values

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

## Reliability

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

## Comments on Preferred Values

10 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

### 15 Rate coefficient data

$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$8.9 \times 10^{-12} (T/298)^{-0.72}$	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)

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## Comments

(a) See comment (a) for  $k_0$ .

(b) See comment (b) for  $k_0$ .

## Preferred Values

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

## Reliability

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

$\Delta n = \pm 0.5$ .

## 10 *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.

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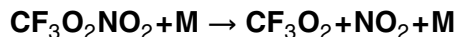
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## IV.A1.63



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

### Low-pressure rate coefficients

#### 5 Rate coefficient data

$k_0/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.5 \times 10^{-5} \exp(-9430/T) [\text{N}_2]$	264–297	Mayer-Figge et al., 1996	(a)

#### Comments

(a) Preparation of  $\text{CF}_3\text{O}_2\text{NO}_2$  by in situ photolysis of  $\text{CF}_3\text{I}/\text{O}_2/\text{NO}_2/\text{N}_2$  mixtures in a 420 l reactor. Time dependence of  $\text{CF}_3\text{O}_2\text{NO}_2$  decay monitored by IR absorption. Measurements in 3.7–1013 mbar of  $\text{N}_2$  evaluated with  $F_c=0.31$ ,  $N_c=1.19$ , and  $k_\infty=1.49 \times 10^{16} \exp(-11940/T) \text{ s}^{-1}$ . Similar results in  $\text{O}_2$ . Analysis of equilibrium constant gives  $\Delta H^\circ=102.7 (\pm 2.0) \text{ kJ mol}^{-1}$ .

#### Preferred Values

$k_0=2.5 \times 10^{-5} \exp(-9430/T) [\text{N}_2] \text{ s}^{-1}$  over the temperature range 260–300 K.

15  $k_0=4.5 \times 10^{-19} [\text{N}_2] \text{ s}^{-1}$  at 298 K.

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## Reliability

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

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

## Comments on Preferred Values

- 5 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  $k_\infty$  such as given in comment (a) for  $k_0$ .

10

## High-pressure rate coefficients

### Rate coefficient data

$k_\infty/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.49 \times 10^{16} \exp(-11940/T)$	264–297	Mayer-Figge et al., 1996	(a)

## Comments

(a) See comment (a) for  $k_0$ .

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## Preferred Values

$k_{\infty}=1.5\times 10^{16} \exp(-11940/T) \text{ s}^{-1}$  over the temperature range 260–300 K.

$k_{\infty}=6.0\times 10^{-2} \text{ s}^{-1}$  at 298 K.

## Reliability

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

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

## Comments on Preferred Values

10 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.

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Destriau, M. and Troe, J.: Int. J. Chem. Kinet., 22, 915, 1990.

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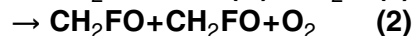
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### Rate coefficient data ( $k = k_1 + k_2$ )

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

### 5 Comments

(a)  $k_{\text{obs}}$  is based on the measured overall second-order decay of  $\text{CH}_2\text{FO}_2$ , defined by  $-\text{d}[\text{CH}_2\text{FO}_2]/\text{dt} = 2k_{\text{obs}} [\text{CH}_2\text{FO}_2]^2$ . As described in detail by Lesclaux (1997),  $\text{HO}_2$  radicals formed from the subsequent chemistry of  $\text{CH}_2\text{FO}$  (formed from channel (2)) are expected to lead to secondary removal of  $\text{CH}_2\text{FO}_2$ . The true value of  $k$  is expected to fall in the range  $k_{\text{obs}}/(1+\alpha) < k < k_{\text{obs}}$ , where  $\alpha = k_2/k$ .

(b) Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{F-O}_2\text{-N}_2$  mixtures at total pressures of 33–533 mbar.  $\text{CH}_2\text{FO}_2$  radicals were monitored by UV absorption with  $\sigma_{240\text{nm}} = (3.72 \pm 0.45) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .

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(c) Pulse radiolysis study of  $\text{CH}_3\text{F-O}_2\text{-SF}_6$  mixtures at a total pressure of 1000 mbar.  $\text{CH}_2\text{FO}_2$  radicals were monitored by UV absorption with  $\sigma_{240\text{ nm}} = (4.11 \pm 0.67) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .

(d)  $\text{CH}_2\text{FO}_2$  radicals were generated from the steady-state photolysis of  $\text{Cl}_2\text{-CH}_3\text{F}$  mixtures at 933 mbar pressure of air. The decay of  $\text{CH}_3\text{F}$  and the formation of products was monitored by FTIR spectroscopy. No  $\text{CH}_2\text{FOH}$  was observed within the detection limits of the apparatus. Significant amounts of  $\text{HC(O)F}$  were observed ( $86 \pm 5\%$ ) and, in experiments with high conversions,  $\text{CH}_2\text{FOOH}$  was observed ( $11 \pm 4\%$ ).

### Preferred Values

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

$k = 2.5 \times 10^{-13} \exp(700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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.

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

$\Delta (k_2/k) = {}^{+0.0}_{-0.2}$  at 298 K.

### Comments on Preferred Values

The product study of Wallington et al. (1992) showed no formation of  $\text{CH}_2\text{FOH}$ , suggesting that channel (1) is negligible at 298 K. The high yields of  $\text{HC(O)F}$  are also consistent with the dominance of channel (2), followed by reaction of  $\text{CH}_2\text{FO}$  with  $\text{O}_2$

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to form HC(O)F and HO<sub>2</sub>. A more recent product study of the CH<sub>2</sub>FO<sub>2</sub>+HO<sub>2</sub> reaction (Wallington et al., 1994) has shown that the only ca. 30% of that reaction produces CH<sub>2</sub>FO<sub>2</sub>H and O<sub>2</sub>, with the remainder forming HC(O)F, H<sub>2</sub>O and O<sub>2</sub>. The low yields of CH<sub>2</sub>FO<sub>2</sub>H observed by Wallington et al. (1992) are thus partially explained by this, but also suggest that HO<sub>2</sub> is probably removed by its self reaction in competition with reaction with CH<sub>2</sub>FO<sub>2</sub>.

The preferred value of  $k$  at 298 K is derived from the  $k_{\text{obs}}$  values reported by Dagaut et al. (1988) and Wallington et al. (1992), adjusted to be consistent with the re-evaluation of  $\sigma_{240\text{ nm}}(\text{CH}_2\text{FO}_2)=4.03\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$  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.  $2\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ ,  $k$  is estimated to be  $k_{\text{obs}}/(1+0.5(k_2/k))$ , with this approximation assuming that the secondary reaction of HO<sub>2</sub> with CH<sub>2</sub>FO<sub>2</sub> competes equally with its removal via HO<sub>2</sub>+HO<sub>2</sub>. The reliability range reflects that  $k$  has been derived by this approximate procedure. The preferred value of  $E/R$  is based on the  $k_{\text{obs}}$  expression of Dagaut et al. (1988). This assumes that the above competition remains valid over the entire temperature range, consistent with the CH<sub>2</sub>FO<sub>2</sub> and HO<sub>2</sub> self reactions, and reaction of CH<sub>2</sub>FO<sub>2</sub> with HO<sub>2</sub> possessing similar temperature dependences.

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

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

#### 5 Comments

(a)  $k_{\text{obs}}$  is based on the measured overall second-order decay of  $\text{CHF}_2\text{O}_2$ , defined by  $-\text{d}[\text{CHF}_2\text{O}_2]/\text{dt} = 2k_{\text{obs}} [\text{CHF}_2\text{O}_2]^2$ . As described in detail by Lesclaux (1997),  $\text{HO}_2$  radicals formed from the subsequent chemistry of  $\text{CHF}_2\text{O}$  (formed from channel (2)) are expected to lead to secondary removal of  $\text{CHF}_2\text{O}_2$ . The true value of  $k$  is expected to fall in the range  $k_{\text{obs}}/(1+\alpha) < k < k_{\text{obs}}$ , where  $\alpha = k_2/k$ .

(b) Pulse radiolysis study of  $\text{CH}_2\text{F}_2\text{-O}_2\text{-SF}_6$  mixtures at a total pressure of 1000 mbar.  $\text{CHF}_2\text{O}_2$  radicals were monitored by UV absorption with  $\sigma_{240\text{nm}} = (2.66 \pm 0.46) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .

(c)  $\text{CHF}_2\text{O}_2$  radicals were generated from the steady-state photolysis of  $\text{Cl}_2\text{-CH}_2\text{F}_2$  mixtures in the presence of air at a total pressure of 933 mbar. The decay of

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CH<sub>2</sub>F<sub>2</sub> and the formation of C(O)F<sub>2</sub> were monitored by FTIR spectroscopy. The yield of C(O)F<sub>2</sub> was 104±2% of the removal of CH<sub>2</sub>F<sub>2</sub>.

### Preferred Values

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

5  $k_2/k \approx 1.0$  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  $k_{\text{obs}}$  with no correction for possible secondary CHF<sub>2</sub>O<sub>2</sub> removal by HO<sub>2</sub> radicals, and the lower limit is a factor of two less than the upper limit, corresponding to a maximum correction for the HO<sub>2</sub> radical reaction.

10 The product study in the same paper (Nielsen et al., 1992) showed that the only carbon-containing product was C(O)F<sub>2</sub>, indicating that channel (2) is the predominant, if not the only, pathway, formed followed by the reaction CHF<sub>2</sub>O+O<sub>2</sub> → C(O)F<sub>2</sub>+HO<sub>2</sub>.  
15 The absence of the product CHF<sub>2</sub>O<sub>2</sub>H expected from the reaction CHF<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub> → CHF<sub>2</sub>O<sub>2</sub>H+O<sub>2</sub>, raises several possibilities, including a slow reaction between CHF<sub>2</sub>O<sub>2</sub> and HO<sub>2</sub> radicals or an alternative reaction pathway, such as CHF<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub> → C(O)F<sub>2</sub>+H<sub>2</sub>O+O<sub>2</sub>. More information is needed on the kinetics and mechanism of the CHF<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub> reaction to define  $k$  and  $k_2/k$  more accurately.

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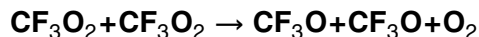
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#### IV.A1.66



$$\Delta H^\circ = -83.2 \text{ kJ mol}^{-1}$$

#### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.8 \pm 0.5) \times 10^{-12}$	295	Nielsen et al., 1992	PR-UVA (a)
$1.8 \times 10^{-12}$	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  $\text{CHF}_3\text{-O}_2\text{-SF}_6$  mixtures at a total pressure of 1000 mbar.  $\text{CF}_3\text{O}_2$  radicals were monitored by UV absorption with  $\sigma_{230 \text{ nm}} = (2.06 \pm 0.40) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ , and an observed rate coefficient,  $k_{\text{obs}} = (3.6 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , was derived from the decay in absorption. Associated FTIR product studies using the photolysis of  $\text{F}_2\text{-CHF}_3\text{-O}_2\text{-N}_2$  mixtures demonstrated quantitative formation of  $\text{CF}_3\text{OOOCF}_3$ , which was explained by the secondary reaction of  $\text{CF}_3\text{O}$  with  $\text{CF}_3\text{O}_2$ . The cited value of  $k$  is thus  $0.5 k_{\text{obs}}$ , to take account of this secondary loss of  $\text{CF}_3\text{O}_2$ .

(b) Flash photolysis of  $\text{CHF}_3\text{-F}_2\text{-O}_2$  mixtures with time-resolved absorption spectroscopy for the detection of  $\text{CF}_3\text{O}_2$  radicals, with  $\sigma_{210 \text{ nm}} = (4.3 \pm 0.3) \times 10^{-18} \text{ cm}^2$

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molecule<sup>-1</sup>. A value of  $k_{\text{obs}} = (3.1 \pm 0.25) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was determined from the time-dependence of the  $\text{CF}_3\text{O}_2$  radical absorbance. The cited value of  $k$  was obtained from a simulation in which secondary removal of  $\text{CF}_3\text{O}_2$  was explicitly represented.

(c) Flash photolysis of  $\text{F}_2$  in the presence of  $\text{N}_2$ ,  $\text{O}_2$ , He, and  $\text{CF}_3\text{CFH}_2$ . Secondary generation of  $\text{CF}_3\text{O}_2$  in the system occurred by the reaction  $\text{CF}_3\text{CHFO} \rightarrow \text{CF}_3 + \text{HCOF}$ , followed by  $\text{CF}_3 + \text{O}_2 + \text{M} \rightarrow \text{CF}_3\text{O}_2 + \text{M}$ .  $\text{CF}_3\text{O}_2$  radicals were monitored by UV absorption, and the 298 K value of  $k_{\text{obs}} = 3.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , 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  $\text{CF}_3\text{O}_2$ . 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  $k_{\text{obs}}$  decreases with increasing temperature.

(d) Experiments performed at pressures in the range 1.3 to 4 mbar.  $\text{CF}_3\text{O}_2$  radicals were produced by the  $\text{F} + \text{CHF}_3$  reaction or the  $\text{F} + \text{CF}_3\text{I}$  reaction, with subsequent addition of  $\text{O}_2$ .  $\text{CF}_3\text{O}_2$  radicals were monitored by titration to  $\text{NO}_2$  following reaction with excess  $\text{NO}$ , with detection of  $\text{NO}_2$  by either LIF or MS. An observed rate coefficient,  $k_{\text{obs}} = (2.0 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , was derived from the decay in  $\text{CF}_3\text{O}_2$ . The cited value of  $k$  was obtained from a simulation in which secondary removal of  $\text{CF}_3\text{O}_2$  was explicitly considered.

(e) Pulse radiolysis study of  $\text{CHF}_3\text{-O}_2\text{-SF}_6$  mixtures at a total pressure of 1000 mbar.  $\text{CF}_3\text{O}_2$  radicals were monitored by UV absorption with  $\sigma_{230\text{nm}} = 3.43 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . The cited value of  $k$  was derived from simulation of the decay in absorption, using a chemical mechanism in which secondary removal of  $\text{CF}_3\text{O}_2$  was explicitly represented.

## Preferred Values

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

## Reliability

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

## 5 Comments on Preferred Values

The reported quantitative formation of  $\text{CF}_3\text{OOOCF}_3$  from  $\text{CHF}_3$  oxidation, in the product study of Nielsen et al. (1992) is consistent with the self-reaction of  $\text{CF}_3\text{O}_2$  proceeding via formation of  $\text{CF}_3\text{O}$  radicals, which react exclusively with  $\text{CF}_3\text{O}_2$ .

10 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  $[\text{CF}_3\text{O}_4\text{CF}_3]^*$  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.  $(1.4 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The observed range in reported  $k$  values  
15 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  $\text{CF}_3\text{O}_2$  absorption cross sections reported by Nielsen and Wallington (1997), which are somewhat lower than those applied by Maricq and Szente (1992a, b) and  
20 Sehested et al. (1997). This leads to respective revised values of  $k$  of  $1.5 \times 10^{-12}$  and  $1.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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

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Biggs et al. (1997). Maricq and Szente (1992b) obtained limited evidence that  $k_{\text{obs}}$  possesses a weak negative temperature coefficient, but further temperature dependence studies are required to quantify this.

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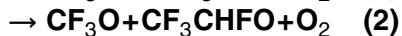
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#### Rate coefficient data ( $k = k_1 + k_2$ )

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

#### 5 Comments

(a) Flash photolysis of  $\text{F}_2$  in the presence of  $\text{CF}_3\text{CH}_2\text{F}-\text{O}_2-\text{N}_2-\text{He}$  mixtures.  $\text{CF}_3\text{CHFO}_2$  radicals were monitored by UV absorption with  $\sigma_{213\text{nm}} = (5.2 \pm 0.3) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . The derived value of  $k$  listed above was obtained by modeling the decay of  $\text{CF}_3\text{CFHO}_2$  radicals and the formation and decay of  $\text{CF}_3\text{O}_2$  radicals.

#### Preferred Values

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

#### Reliability

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

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## 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  $\text{CF}_3\text{O}_2$  and  $\text{CF}_3\text{CHFO}_2$  radicals.

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

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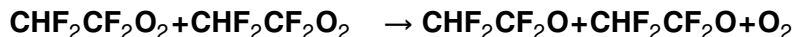
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## IV.A1.68



### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = (2.7 \pm 0.6) \times 10^{-12}$	298	Nielsen et al., 1992a	PR-UVA (a)

### 5 Comments

(a) Pulse radiolysis study of  $\text{CHF}_2\text{CHF}_2\text{-O}_2\text{-SF}_6$  mixtures at a total pressure of 1000 mbar.  $\text{CHF}_2\text{CF}_2\text{O}_2$  radicals were monitored by UV absorption with  $\sigma_{230} = (3.2 \pm 0.5) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .  $k_{\text{obs}}$  is based on the measured overall second-order decay in absorption at 230 nm, which was defined as  $-\text{d}[\text{CHF}_2\text{CF}_2\text{O}_2]/\text{dt} = 2k_{\text{obs}}[\text{CHF}_2\text{CF}_2\text{O}_2]^2$ . Product studies were also performed on the steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CHF}_2\text{CHF}_2\text{-air}$  mixtures at 933 mbar total pressure. The decay of  $\text{CHF}_2\text{CHF}_2$  and the formation of  $\text{COF}_2$ , the only carbon-containing product observed, were monitored by FTIR spectroscopy. The yield of  $\text{COF}_2$  was  $98 \pm 2\%$  relative to the decay of  $\text{CHF}_2\text{CHF}_2$ .

### 15 Preferred Values

No recommendation

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## Comments on Preferred Values

Although the value of  $k_{\text{obs}}$  reported by Nielsen et al. (1992a) is likely to be indicative of the magnitude of the self-reaction rate coefficient for  $\text{CHF}_2\text{CF}_2\text{O}_2$ , the probable formation of  $\text{CHF}_2\text{O}_2$  and  $\text{HO}_2$  radicals from the subsequent chemistry (see below) is expected to lead to secondary removal of  $\text{CHF}_2\text{CF}_2\text{O}_2$ , 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  $k_{\text{obs}}$ , 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  $\text{COF}_2$  from the oxidation of  $\text{CHF}_2\text{CHF}_2$ , consistent with exclusive formation of  $\text{CHF}_2\text{CF}_2\text{O}$  from the self-reaction of  $\text{CHF}_2\text{CF}_2\text{O}_2$ , followed by decomposition to form  $\text{COF}_2$  and  $\text{CHF}_2$ . The  $\text{CHF}_2$  radicals form  $\text{CHF}_2\text{O}_2$  radicals, which are known (Nielsen et al., 1992b) to interact via their self-reaction, resulting in the formation of  $\text{COF}_2$  and  $\text{HO}_2$  from the subsequent reaction of  $\text{CHF}_2\text{O}$  with  $\text{O}_2$ . However, it is probable that  $\text{CHF}_2\text{O}_2$  is also converted to  $\text{CHF}_2\text{O}$  via reaction with  $\text{CHF}_2\text{CF}_2\text{O}_2$  in the system.  $\text{HO}_2$  radicals, generated from  $\text{CHF}_2\text{O} + \text{O}_2$ , potentially also react with both  $\text{CHF}_2\text{CF}_2\text{O}_2$  and  $\text{CHF}_2\text{O}_2$ , in competition with their self-reaction. The absence of the products  $\text{CHF}_2\text{CF}_2\text{O}_2\text{H}$  and  $\text{CHF}_2\text{O}_2\text{H}$ , which might be formed in these reactions, raises several possibilities: the reactions of  $\text{HO}_2$  with  $\text{CHF}_2\text{CF}_2\text{O}_2$  and  $\text{CHF}_2\text{O}_2$  may be too slow to compete with the self-reaction, or they may proceed by alternative pathways leading to  $\text{COF}_2$  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.

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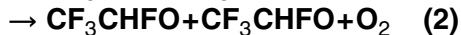
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#### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$7.8 \times 10^{-13} \exp[(605 \pm 40)/T]$	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)
<i>Branching Ratios</i>			
$k_1/k = 0.28$	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		

#### 5 Comments

(a)  $k$  is defined by  $-d[\text{CF}_3\text{CHFO}_2]/dt = 2k[\text{CF}_3\text{CHFO}_2]^2$ .

(b) Flash photolysis of  $\text{F}_2$  in the presence of  $\text{N}_2$ ,  $\text{O}_2$ , He and  $\text{CF}_3\text{CH}_2\text{F}$ .  $\text{CF}_3\text{CHFO}_2$  radicals were monitored by UV absorption with  $\sigma_{240 \text{ nm}} = (5.2 \pm 0.3) \times 10^{-13} \text{ cm}^2 \text{ molecule}^{-1}$ . The derived value of  $k$  listed above was obtained by modelling the decay curves for  $\text{CF}_3\text{CHFO}_2$  radicals with a mechanism of 9 reactions.

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(c) Pulse radiolysis study of  $\text{CF}_3\text{CH}_2\text{F}-\text{O}_2-\text{SF}_6$  mixtures at a total pressure of 1000 mbar.  $\text{CF}_3\text{O}_2$  radicals were monitored by UV absorption at 220 nm ( $\sigma=5.34\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ ), 230 nm ( $\sigma=4.50\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ ) and 240 nm ( $\sigma=3.06\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ ). The cited value of  $k$  was derived from simulation of the decay in absorption, using a chemical mechanism in which secondary removal of  $\text{CF}_3\text{CHFO}_2$  was explicitly represented.

(d) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CF}_3\text{CFH}_2-\text{O}_2$  mixtures at a total pressure of 933 mbar with FTIR analysis of the products  $\text{HC}(\text{O})\text{F}$  and  $\text{CF}_3\text{C}(\text{O})\text{F}$ . The branching ratio was determined from the yields of  $\text{CF}_3\text{C}(\text{O})\text{F}$  as a function of added  $\text{O}_2$ , extrapolated to zero  $\text{O}_2$  partial pressure.

(e) Similar experiments to those of Comment (d). The branching ratios were derived from the yields of  $\text{CF}_3\text{C}(\text{O})\text{F}$  in the presence of 787 mbar  $\text{N}_2$  and 1.3 mbar  $\text{O}_2$ .

**Preferred Values**

$k=4.7\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

$k=6.2\times 10^{-13}\exp(605/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  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.

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

$\Delta(k_1/k)=\Delta(k_2/k)=\pm 0.05$  over the temperature range 270–350 K.

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## 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.

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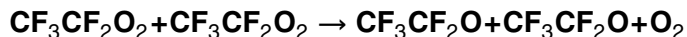
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### Rate coefficient data

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

### Comments

(a) Pulse radiolysis study of  $\text{CF}_3\text{CHF}_2\text{-O}_2\text{-SF}_6$  mixtures at a total pressure of 1000 mbar.  $\text{CF}_3\text{CF}_2\text{O}_2$  radicals were monitored by UV absorption with  $\sigma_{230\text{ nm}} = (2.74 \pm 0.46) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .  $k_{\text{obs}}$  is based on the measured overall second-order decay in absorption at 230 nm, which was defined as  $-\text{d}[\text{CF}_3\text{CF}_2\text{O}_2]/\text{dt} = 2k_{\text{obs}}[\text{CF}_3\text{CF}_2\text{O}_2]^2$ . Products studies were also performed on the steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CF}_3\text{CHF}_2\text{-air}$  mixtures at 933 mbar total pressure. The decay of  $\text{CF}_3\text{CHF}_2$  and the formation of products were monitored by FTIR spectroscopy. The observed products were  $\text{C(O)F}_2$ ,  $\text{CF}_3\text{O}_3\text{CF}_3$  and  $\text{CF}_3\text{O}_3\text{C}_2\text{F}_5$ , and accounted for 100% of the  $\text{CF}_3\text{CF}_2\text{H}$  loss.

### Preferred Values

No recommendation

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## Comments on Preferred Values

Although the value of  $k_{\text{obs}}$  reported by Sehested et al. (1993) is likely to be indicative of the magnitude of the self-reaction rate coefficient for  $\text{CF}_3\text{CF}_2\text{O}_2$ , the formation of  $\text{CF}_3\text{O}_2$  and  $\text{CF}_3\text{O}$  radicals from the subsequent chemistry (see below) leads to secondary removal of  $\text{CF}_3\text{CF}_2\text{O}_2$ , but also interferences in the absorption traces at 230 nm, because the spectra for  $\text{CF}_3\text{CF}_2\text{O}_2$  and  $\text{CF}_3\text{O}_2$  are almost identical. These two factors have opposing influences on  $k_{\text{obs}}$ , 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  $\text{C}(\text{O})\text{F}_2$  observed in the product study of Sehested et al. (1993) is consistent with exclusive formation of  $\text{CF}_3\text{CF}_2\text{O}$  from the self-reaction of  $\text{CF}_3\text{CF}_2\text{O}_2$ , followed by decomposition to form  $\text{C}(\text{O})\text{F}_2$  and  $\text{CF}_3$ . The  $\text{CF}_3$  radicals form  $\text{CF}_3\text{O}_2$  radicals, which are known (Nielsen et al., 1992) to interact via their self-reaction, resulting in the formation of  $\text{CF}_3\text{O}$ . However, it is probable that  $\text{CF}_3\text{O}_2$  is also converted to  $\text{CF}_3\text{O}$  via reaction with  $\text{CF}_3\text{CF}_2\text{O}_2$  in the system. Further removal of both  $\text{CF}_3\text{CF}_2\text{O}_2$  and  $\text{CF}_3\text{O}_2$  occurs via their reactions with  $\text{CF}_3\text{O}$ , which lead to the observed products  $\text{CF}_3\text{O}_3\text{C}_2\text{F}_5$  and  $\text{CF}_3\text{O}_3\text{CF}_3$  (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.

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- Nielsen, O. J., Ellermann, T., Sehested, J., Bartkiewicz, E., Wallington, T. J., and Hurley, M. D.: *Int. J. Chem. Kinet.*, 24, 1009, 1992.
- Sehested, J., Ellermann, T., Nielsen, O. J., Wallington, T. J., and Hurley, M. D.: *Int. J. Chem. Kinet.* 25, 701, 1993.

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

## Primary photochemical transitions

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

## 5 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  $\sigma = 6.65 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$  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 16558

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structured absorption at 268 nm and a maximum of intensity near 210 nm. The maximum value of  $\sigma=1.5\times 10^{-19}\text{ cm}^2\text{ molecule}^{-1}$  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  $501\text{ mol}^{-1}\text{ cm}^{-1}$  ( $\sigma=1.9\times 10^{-19}\text{ cm}^2\text{ molecule}^{-1}$ ) at the maximum.

### Quantum Yield Data

There are no reported quantum yield data. Klimeck and Berry (1973) have observed infrared laser emission from  $\text{HF}^*$  following flash photolysis of  $\text{HC(O)F}$  ( $\lambda>165\text{ nm}$ ), 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  $\sim 243\text{-}247\text{ nm}$ .

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## Preferred Values

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

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
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				

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## 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.

Klimeck, E. and Berry, M. J.: Chem. Phys. Lett., 20, 141, 1973.

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.

Meller, R. and Moortgat, G.: Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere, Final Report to STEP-0004-C(EDB), 1992.

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.

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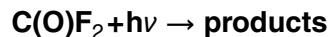
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### Primary photochemical transitions

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
C(O)F <sub>2</sub> +hν	→ FCO+F (1)	562	213
	→ CO+2F (2)	683	175
	→ CF <sub>2</sub> +O( <sup>3</sup> P) (3)	700	171

### 5 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<sub>2</sub> pressures of 10-30 mbar. Because of the high concentrations of FCO radicals in the laser photolysis experiments, formation of C(O)F<sub>2</sub> was assumed to occur via the reaction FCO+FCO → C(O)F<sub>2</sub>+CO as observed in analogous experiments with C(O)FCl (Nölle et al.,

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1999). Therefore, the cited quantum yield is the measured value ( $0.47 \pm 0.03$ ) corrected for reformation of  $\text{C}(\text{O})\text{F}_2$  from the FCO radical self-reaction.

(b) Photolysis at 298K using a medium pressure mercury lamp-monochromator combination, with initial  $\text{C}(\text{O})\text{F}_2$  pressures of 2.1–6.3 mbar. Because of the low concentrations of FCO radicals in these experiments, reformation of  $\text{C}(\text{O})\text{F}_2$  from the reaction  $\text{FCO} + \text{FCO} \rightarrow \text{C}(\text{O})\text{F}_2 + \text{CO}$  was not anticipated to be significant, as confirmed by observations in analogous experiments with  $\text{C}(\text{O})\text{FCl}$  (Nölle et al., 1999). Therefore, the cited quantum yield is the measured value.

(c) With added  $\text{N}_2$  diluent gas at pressures of 600–1000 mbar.

## Preferred Values

### Absorption cross-sections for $\text{C}(\text{O})\text{F}_2$ photolysis at 298 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
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

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## Quantum Yields for C(O)F<sub>2</sub> 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

5

### *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<sup>-1</sup> intervals. Nölle et al. (1992; 1999) photolyzed C(O)F<sub>2</sub> at three wavelengths in the range 193–220 nm. The overall quantum yield for loss of C(O)F<sub>2</sub>, which must be through channel (1), decreases monotonically with increasing wavelength. In the absence of confirmatory data, the quantum yields measured by Nölle et al. (1992; 1999) are recommended.

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### 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.

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**CF<sub>3</sub>CHO+hν → products****Primary photochemical transitions**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF <sub>3</sub> CHO+hν → CF <sub>3</sub> +HCO (1)		
→ CF <sub>3</sub> CO+H (2)		
→ CHF <sub>3</sub> +CO (3)		

5 **Absorption cross-section data**

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

**Quantum yield data**

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

**Comments**

- 10 (a) Absolute absorption cross-sections were measured using a diode-array spectrometer over the temperature range 240–300 K. The UV spectrum of trifluoroac-16565

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etaldehyde shows a broad band, centered at 305 nm and extending out to 355 nm. Values of  $\sigma$  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  $298 \pm 2$  K, at a spectral resolution of 2 nm. The UV spectrum of trifluoroacetaldehyde shows a broad band, centered at  $\sim 300$  nm and extending out to  $\geq 355$  nm. Values of  $\sigma$  were given at 5 nm intervals at 298 K.
- (c) Photolysis of  $\text{CF}_3\text{CHO}$  in pure air in the presence of an OH radical tracer (di-*n*-butyl ether) in the  $\sim 200 \text{ m}^3$  EUPHORE chamber facility under natural sunlight conditions. The measured first-order loss rate of  $\text{CF}_3\text{CHO}$  during a  $\sim 3$  hr period around solar noon was  $7.74 \times 10^{-6} \text{ s}^{-1}$ , essentially identical to the leak obtained from monitoring the decay of  $\text{SF}_6$ . After correction for the leak rate and reaction with OH radicals, the calculated first-order loss rate of  $\text{CF}_3\text{CHO}$  due to photolysis during this  $\sim 3$  hr period was  $< 8.5 \times 10^{-7} \text{ s}^{-1}$ , compared to the calculated photolysis rate of  $5.5 \times 10^{-5} \text{ s}^{-1}$  using a unit quantum yield for photodissociation.

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## Preferred Values

### Absorption cross-sections of CF<sub>3</sub>CHO at 298 K

$\lambda/\text{nm}$	$10^{21} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{21} \sigma/\text{cm}^2$
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		

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## Quantum Yields of CF<sub>3</sub>CHO

No recommendation.

### *Comments on Preferred Values*

The preferred values for the cross-sections are based on the data reported by Sellevåg et al. (2004), which are ~7% higher than the data of Meller et al. (1993) at the peak absorption at ~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 Sellevåg 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<sub>3</sub>CHO have been investigated by Dodd and Watson-Smith (1957). More recently, Richer et al. (1993) have studied the photooxidation of CF<sub>3</sub>CHO and observed CHF<sub>3</sub>, CO, CO<sub>2</sub> and COF<sub>2</sub> as products. Photodissociation appears to occur predominantly via reaction (1). However, Richer et al. (1993) observed substantial yields (14%) of CHF<sub>3</sub> in the 254 nm photolysis of CF<sub>3</sub>CHO in air, indicating that channel (3) also occurs at that wavelength.

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Dodd, R. E. and Watson-Smith, J.: J. Chem. Soc., 1465, 1957.

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.

Richer, H., Sodeau, J. R., and Barnes, I.: Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere, STEP-HALOCSIDE/AFEAS

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Sellevåg, S. R., Sidebottom, H.- and Nielsen, C. J.: Phys. Chem. Chem. Phys., 6, 1243, 2004.

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### Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_3\text{C}(\text{O})\text{F} + h\nu \rightarrow \text{CF}_3 + \text{CFO}$ (1)		
$\rightarrow \text{CF}_3\text{CO} + \text{F}$ (2)		

### 5 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

- 10 (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  
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trifluoroacetyl fluoride shows a single band extending out to 300 nm, where there is significant temperature dependence, Values of  $\sigma$  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.

- 5 (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  $\text{CF}_3\text{C}(\text{O})\text{F}$  by photolysis in 1 atm air at 298 K, relative to the loss of  $\text{C}(\text{O})\text{Cl}_2$ , for which  $\Phi=1$ .
- 10 (d) Measurement of the overall loss of  $\text{CF}_3\text{C}(\text{O})\text{F}$  in the presence of  $\text{O}_2$  (0.67–6.7 mbar) at 298 K.

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## Preferred Values

### Absorption cross-sections of CF<sub>3</sub>C(O)F at 293K and 238 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 293K	$10^{20} \sigma/\text{cm}^2$ 238K	$10^3 \text{ B/K}^{-1a}$
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	

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

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## Quantum Yields of CF<sub>3</sub>C(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

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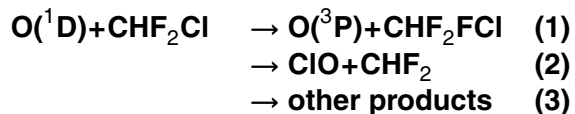
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## Appendix 2: ClO<sub>x</sub> Reactions

### IV.A2.75



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

$$5 \quad \Delta H^\circ(2) = -92 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(0.95 \pm 0.3) \times 10^{-10}$	173-343	Davidson et al., 1978	PLP (a)
$(1.08 \pm 0.20) \times 10^{-10}$	298	Warren et al., 1991	PLP-RF
<i>Branching Ratios</i>			
$k_1/k = 0.28 \pm 0.06$	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<sub>3</sub> at 266 nm. O(<sup>1</sup>D) atoms were monitored by time-resolved emission at 630 nm.

(b) Branching ratio was determined from the ratio of the O(<sup>3</sup>P) yield from O(<sup>1</sup>D) + CHF<sub>2</sub>Cl relative to that for O(<sup>1</sup>D) + N<sub>2</sub>.

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

### Preferred Values

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

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

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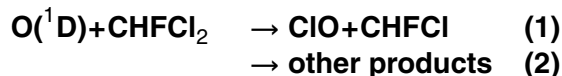
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## IV.A2.76



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

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

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

### Comments

(a) Pulsed laser photolysis of  $\text{O}_3$  at 266 nm.  $\text{O}(^1\text{D})$  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  $\text{O}(^1\text{D}) + \text{HCl}$ .

### Preferred Values

$k = 1.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  independent of temperature over the range 180–350 K.

$k_1/k = 0.74$  at 298 K.

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## 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

- 5 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.

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

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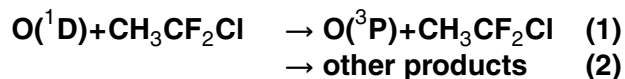
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## IV.A2.77



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

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

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

### Comments

(a) Branching ratio was determined from the ratio of the  $\text{O}(^3\text{P})$  yield from  $\text{O}(^1\text{D}) + \text{CH}_3\text{CF}_2\text{Cl}$  relative to that for  $\text{O}(^1\text{D}) + \text{N}_2$ .

### Preferred Values

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

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## Reliability

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

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

## Comments on Preferred Values

- 5 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  $O(^1D) + CH_3CF_2Cl$  was obtained.

## References

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

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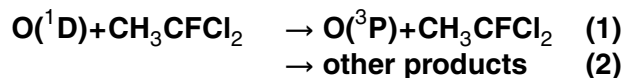
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## IV.A2.78



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

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

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

### Comments

(a) Branching ratio was determined from the ratio of the  $\text{O}(^3\text{P})$  yield from  $\text{O}(^1\text{D}) + \text{CH}_3\text{CFCl}_2$  relative to that for  $\text{O}(^1\text{D}) + \text{N}_2$ .

### Preferred Values

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

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## Reliability

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

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

## Comments on Preferred Values

- 5 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  $O(^1D) + CH_3CFCl_2$  was obtained.

## References

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

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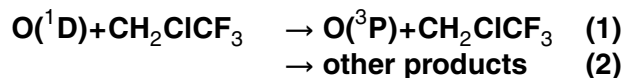
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## IV.A2.79



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

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

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

### Comments

(a) Branching ratio was determined from the ratio of the  $\text{O}(^3\text{P})$  yield from  $\text{O}(^1\text{D}) + \text{CH}_2\text{ClCF}_3$  relative to that for  $\text{O}(^1\text{D}) + \text{N}_2$ .

### Preferred Values

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

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## Reliability

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

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

## Comments on Preferred Values

- 5 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  $O(^1D) + CH_2ClCF_3$  was obtained.

## References

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

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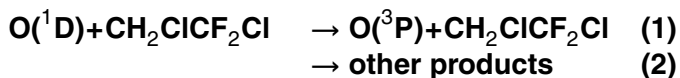
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## IV.A2.80



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

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<sup>5</sup> <i>Absolute Rate Coefficients</i>			
$k_2 = (1.6 \pm 0.6) \times 10^{-10}$	297	Green and Wayne, 1976	RR (a)

### Comments

(a)  $\text{O}(^1\text{D})$  produced by photolysis of  $\text{NO}_2$  at 229 nm.  $\Delta(\text{CH}_2\text{ClCF}_2\text{Cl})/\Delta(\text{N}_2\text{O})$  monitored by IR absorption spectroscopy. Measured rate coefficient ratio of  $k_2/k(\text{O}(^1\text{D}) + \text{N}_2\text{O}) = 1.4 \pm 0.3$  is placed on an absolute basis by use of  $k(\text{O}(^1\text{D}) + \text{N}_2\text{O}) = 1.16 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current evaluation). The cited rate coefficient refers to chemical reaction only and does not include physical quenching.

### Preferred Values

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

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## Reliability

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

## Comments on Preferred Values

5 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  $O(^1D)$ .

## References

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

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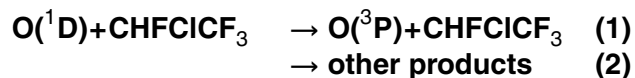
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## IV.A2.81



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

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

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

### Comments

(a) Branching ratio was determined from the ratio of the  $\text{O}(^3\text{P})$  yield from  $\text{O}(^1\text{D}) + \text{CHFClCF}_3$  relative to that for  $\text{O}(^1\text{D}) + \text{N}_2$ .

### Preferred Values

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

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## Reliability

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

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

## Comments on Preferred Values

- 5 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  $O(^1D) + \text{CHFClCF}_3$  was obtained.

## References

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

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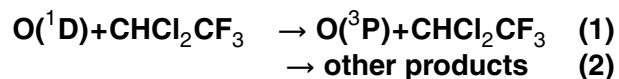
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## IV.A2.82



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

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

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

### Comments

(a) Branching ratio was determined from the ratio of the  $\text{O}(^3\text{P})$  yield from  $\text{O}(^1\text{D}) + \text{CHCl}_2\text{CF}_3$  relative to that for  $\text{O}(^1\text{D}) + \text{N}_2$ .

### Preferred Values

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

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## Reliability

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

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

## Comments on Preferred Values

- 5 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  $O(^1D) + CHCl_2CF_3$  was obtained.

## References

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

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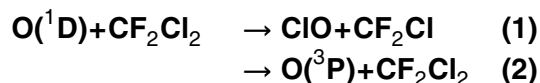
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## IV.A2.83



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

$$\Delta H^\circ(2) = -190 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.45 \pm 0.5) \times 10^{-10}$	173-343	Davidson et al., 1978	PLP (a)
$(1.4 \pm 0.2) \times 10^{-10}$	298	Force and Wiesenfeld, 1981	PLP-RA
<i>Branching Ratios</i>			
$k_2/k = 0.14 \pm 0.07$	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  $\text{O}_3$  at 266 nm.  $\text{O}(^1\text{D})$  atoms were monitored by time-resolved emission at 630 nm.

10 (b)  $\text{O}(^1\text{D})$  atoms were monitored by resonance absorption at 130.4 nm and compared to  $\text{O}(^3\text{P})$  atoms in the presence of ozone in He diluent where the  $\text{O}(^3\text{P})$  atom yield from the  $\text{O}(^1\text{D}) + \text{O}_3$  reaction is 1.0.

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

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

## 5 Preferred Values

$k=1.4\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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.

## 10 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

15 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  
20 sum of the two preferred branching ratios equal to unity.

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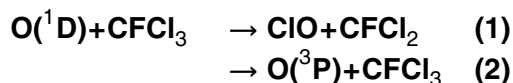
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## IV.A2.84



$$\begin{aligned} \Delta H^\circ(1) &= -142 \text{ kJ mol}^{-1} \\ \Delta H^\circ(2) &= -190 \text{ kJ mol}^{-1} \end{aligned}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.2 \pm 0.7) \times 10^{-10}$	173-343	Davidson et al., 1978	PLP (a)
$(2.4 \pm 0.2) \times 10^{-10}$	298	Force and Wiesenfeld, 1981	PLP-RA
<i>Branching Ratios</i>			
$k_2/k = 0.13 \pm 0.05$	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  $\text{O}_3$  at 266 nm.  $\text{O}(^1\text{D})$  atoms were monitored by time-resolved emission at 630 nm.

10 (b)  $\text{O}(^1\text{D})$  atoms were monitored by resonance absorption at 130.4 nm and compared to  $\text{O}(^3\text{P})$  atoms in the presence of ozone in He diluent where the  $\text{O}(^3\text{P})$  atom yield from the  $\text{O}(^1\text{D}) + \text{O}_3$  reaction is 1.0.

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(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

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

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

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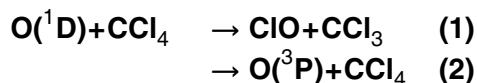
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## IV.A2.85



$$\Delta H^\circ(1) = -170 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -190 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.1 \pm 0.9) \times 10^{-10}$	203-343	Davidson et al., 1978	PLP (a)
$(3.5 \pm 0.3) \times 10^{-10}$	298	Force and Wiesenfeld, 1981	PLP-RA
<i>Branching Ratios</i>			
$k_2/k = 0.14 \pm 0.06$	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  $\text{O}_3$  at 266 nm.  $\text{O}(^1\text{D})$  atoms were monitored by time-resolved emission at 630 nm.

10 (b)  $\text{O}(^1\text{D})$  atoms were monitored by resonance absorption at 130.4 nm and compared to  $\text{O}(^3\text{P})$  atoms in the presence of ozone in He diluent where the  $\text{O}(^3\text{P})$  atom yield from the  $\text{O}(^1\text{D}) + \text{O}_3$  reaction is 1.0.

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

### Preferred Values

$k = 3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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.

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Davidson, J. A., Schiff, H. I., Brown, T. J., and Howard, C. J.: J. Chem. Phys., 69, 4277, 1978.

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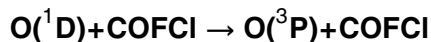
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## IV.A2.86



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

### 5 Rate coefficient data

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

### Comments

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

### 10 Preferred Values

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

### Reliability

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

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## Comments on Preferred Values

The preferred value is 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(<sup>1</sup>D) rate studies suggests that O(<sup>1</sup>D) rates reported by Husain and co-workers contain a systematic error, and that these results can be made consistent with other O(<sup>1</sup>D) 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.

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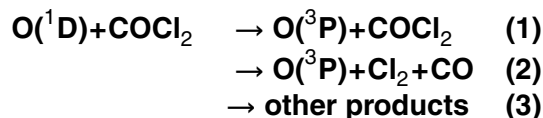
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## IV.A2.87



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

$$\Delta H^\circ(2) = -80 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.6 \pm 0.5) \times 10^{-10}$	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		
<i>Branching Ratios</i>			
$(k_1 + k_2)/k = 0.20 \pm 0.04$	194-429	Strekowski et al., 2000	PLP-RF (a)

### Comments

(a) Branching ratio for conversion of  $\text{O}(^1\text{D})$  to  $\text{O}(^3\text{P})$ , i.e.  $(k_1 + k_2)/k$  was determined by comparison of the  $\text{O}(^3\text{P})$  yield from  $\text{O}(^1\text{D}) + \text{COCl}_2$  relative to that for  $\text{O}(^1\text{D}) + \text{N}_2$ .

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## Preferred Values

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

$k=2.0\times 10^{-10}\exp(25/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 190–430 K.

$(k_1+k_2)/k=0.20$ .

### 5 **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**

10 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.

### 15 **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.

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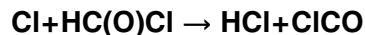
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## Rate coefficient data

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

## 5 Comments

(a) Rate coefficient ratios of  $k(\text{Cl} + \text{HC(O)Cl})/k(\text{Cl} + \text{CH}_3\text{Cl}) = 1.85 \pm 0.43$  and  $k(\text{Cl} + \text{HC(O)Cl})/k(\text{Cl} + \text{CH}_2\text{Cl}_2) = 1.66 \pm 0.15$  derived from the kinetic analysis of HC(O)Cl in Cl atom-sensitized oxidation of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>Cl. This was placed on an absolute basis by use of  $k(\text{Cl} + \text{CH}_3\text{Cl}) = 5.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{Cl} + \text{CH}_2\text{Cl}_2) = 3.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (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  $k(\text{Cl} + \text{HC(O)Cl})/k(\text{Cl} + \text{CH}_3\text{Cl}) = 1.6 \pm 0.2$  determined using FTIR absorption spectroscopy in irradiated Cl<sub>2</sub>-CH<sub>3</sub>Cl-O<sub>2</sub>-N<sub>2</sub> mixtures at 933 mbar total pressure. The rate coefficient ratio was placed on an absolute

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basis by use of  $k(\text{Cl}+\text{CH}_3\text{Cl})=4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(c) Relative rate study. Cl atoms generated by the photolysis of  $\text{Cl}_2$  in  $\text{Cl}_2$ - $\text{HC}(\text{O})\text{Cl}$ - $\text{CH}_4$ - $\text{N}_2$  mixtures at 1000 mbar total pressure. The concentrations of  $\text{HC}(\text{O})\text{Cl}$  and  $\text{CH}_4$  were measured by FTIR absorption spectroscopy ( $\text{HC}(\text{O})\text{Cl}$ ) and/or gas chromatography ( $\text{CH}_4$ ). Rate coefficient ratios were determined over the temperature range 265.8–321.3 K, and placed on an absolute basis by use of  $k(\text{Cl}+\text{CH}_4)=6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(d) Temperature dependent rate coefficient ratios of  $k(\text{Cl}+\text{HC}(\text{O})\text{Cl})/k(\text{Cl}+\text{CH}_2\text{Cl}_2)$  were derived from the kinetic analysis of  $\text{HC}(\text{O})\text{Cl}$  in Cl atom-sensitized oxidation of  $\text{CH}_2\text{Cl}_2$ . Placed on an absolute basis by use of  $k(\text{Cl}+\text{CH}_2\text{Cl}_2)=5.9 \times 10^{-12} \exp(-850/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation). The value of  $k$  at 298 K was taken from the Arrhenius expression presented.

### Preferred Values

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

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

### Reliability

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

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

## 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.

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IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>, 2007.

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.

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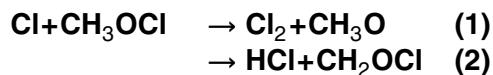
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## IV.A2.89



$$\Delta H^\circ(1) = -39.7 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -14.2 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.0 \pm 0.2) \times 10^{-11}$	300	Kukui et al., 1997	DF-MS/LIF (a)
<i>Relative Rate Coefficients</i>			
$(6.3 \pm 0.1) \times 10^{-11}$	295	Carl et al., 1996	RR (b)
<i>Branching Ratios</i>			
$k_1/k = 0.8 \pm 0.2$	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<sub>2</sub> monitored as their parent ions, CH<sub>3</sub>O was monitored by LIF, but not quantified. The relative sensitivity of the MS to Cl and Cl<sub>2</sub> was determined by titration of Cl to Cl<sub>2</sub> via reaction with NOCl. Rate coefficients were obtained from the Cl decay in excess CH<sub>3</sub>OCl, and

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the branching ratio,  $k_1/k$ , was derived by numerical modeling of Cl loss and Cl<sub>2</sub> production processes both in the desired reaction and secondary processes.

(b) Relative rates of removal of CH<sub>3</sub>OCl and C<sub>2</sub>H<sub>6</sub> (reference reactant) monitored by FTIR in air and N<sub>2</sub> bath gas at total pressure of 133 to 988 mbar. The value  $k/k(\text{Cl}+\text{C}_2\text{H}_6)=1.07\pm 0.02$  was combined with the IUPAC (2007) recommendation for  $k(\text{Cl}+\text{C}_2\text{H}_6)$  to yield the value for  $k$  listed in the table.

(c) Branching ratios determined by quantitative analysis of CH<sub>3</sub>OCl loss combined with HCl formation (FTIR experiments) and also by CH<sub>3</sub>OCl loss combined with Cl<sub>2</sub> formation (UV experiments). The chemistry was initiated by photolysis of Cl<sub>2</sub> or CH<sub>3</sub>OCl itself. The HCl formation was modeled to assess the effects of secondary reactions such as Cl+HCHO.

### Preferred Values

$k=6.1\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  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.

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## 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 efficiencies at room temperature and dominance of hydrogen abstraction at higher temperatures (He et al., 2005).

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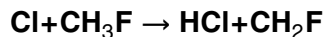
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$$\Delta H^\circ = -12.8 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.1 \times 10^{-12} \exp[-(790 \pm 45)/T]$	216–296	Manning and Kurylo, 1977	FP-RF (a)
$3.6 \times 10^{-13}$	298		
$(2.7 \pm 0.2) \times 10^{-13}$	298	Hitsuda et al., 2001	PLP-LIF (b)
<i>Relative Rate Coefficients</i>			
$1.3 \times 10^{-11} \exp(-1050/T)$	273–368	Tschuikow-Roux et al., 1988	RR (c)
$3.8 \times 10^{-13}$	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  $\text{CCl}_4$ . The Arrhenius expression was derived by least squares fitting to tabulated data, excluding those in which  $\text{CH}_3\text{F}$  was excited by  $\text{CO}_2$  laser.

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

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(c) Cl atoms were generated by the photolysis of Cl<sub>2</sub>. Product yield ratios were measured by GC. Derived values of  $A/A_{\text{CH}_4}=(2.02\pm 0.01)$  and  $(E-E_{\text{CH}_4})/R=(-190\pm 6)$  K are placed on an absolute basis using  $k(\text{Cl}+\text{CH}_4)=6.6\times 10^{-12}\exp(-1240/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation).

(d) Cl atoms were generated by the photolysis of Cl<sub>2</sub>. 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  $k(\text{Cl}+\text{CH}_4)=1.0\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation).

(e) Cl atoms were generated by the photolysis of Cl<sub>2</sub>. 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  $k(\text{Cl}+\text{CH}_4)=1.0\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

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

$k=4.0\times 10^{-12}\exp(-730/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  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

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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).

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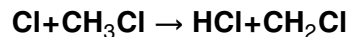
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$$\Delta H^\circ = -14.3 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.1 \times 10^{-10} \exp[(-1790 \pm 70)/T]$	300–604	Clyne and Walker, 1973	DF-MS
$5.4 \times 10^{-13}$	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		
<i>Relative Rate Coefficients</i>			
$(4.8 \pm 0.4) \times 10^{-13}$	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)
$4.7 \times 10^{-13}$	298		

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## Comments

(a) Cl atoms were generated from the photolysis of  $\text{Cl}_2$  in  $\text{Cl}_2$ - $\text{CH}_3\text{Cl}$ - $\text{CH}_4$  air mixtures at 930 mbar total pressure. The concentrations of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_4$  were monitored by FTIR absorption spectroscopy and a rate coefficient ratio  $k(\text{Cl}+\text{CH}_3\text{Cl})/k(\text{Cl}+\text{CH}_4)=4.79\pm 0.39$  determined. This was placed on an absolute basis by use of  $k(\text{Cl}+\text{CH}_4)=1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(b) Cl atoms were generated from the photolysis of  $\text{Cl}_2$  in  $\text{Cl}_2$ - $\text{CH}_3\text{Cl}$ - $\text{CH}_4$  mixtures at atmospheric pressure of  $\text{N}_2$ , air or Ar. The concentrations of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_4$  were monitored by GC and a rate coefficient ratio  $k(\text{Cl}+\text{CH}_3\text{Cl})/k(\text{Cl}+\text{CH}_4)=4.65\pm 0.57$  was determined. This was placed on an absolute basis by use of  $k(\text{Cl}+\text{CH}_4)=1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(c) Cl atoms were generated from the photolysis of  $\text{Cl}_2$  in  $\text{Cl}_2$ - $\text{CH}_3\text{Cl}$ - $\text{CH}_4$  mixtures at 930 mbar total pressure of  $\text{O}_2$ - $\text{N}_2$ . The concentrations of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_4$  were monitored by FTIR absorption spectroscopy and a temperature dependent rate coefficient ratio  $k(\text{Cl}+\text{CH}_3\text{Cl})/k(\text{Cl}+\text{CH}_4)$  determined. This was placed on an absolute basis by use of  $k(\text{Cl}+\text{CH}_4)=6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation). The results were consistent with those obtained using  $\text{CH}_3\text{Br}$  as reference reactant.

## Preferred Values

$k=4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k=2.3 \times 10^{-11} \exp(-1150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220–360 K.

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## Reliability

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

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

## Comments on Preferred Values

5 The 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  
10 360 K where these data sets are in very good agreement.

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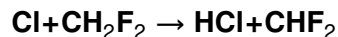
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$$\Delta H^\circ = 0.5 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$1.0 \times 10^{-11} \exp(-1470/T)$	281-368	Tschuikow-Roux et al., 1985	RR (a)
$7.3 \times 10^{-14}$	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  $\text{Cl}_2$ . Product yield ratios were measured by GC. Derived values of  $A/A_{\text{CH}_4} = (1.51 \pm 0.06)$  and  $(E - E_{\text{CH}_4})/R = (228 \pm 12) \text{ K}$  were placed on an absolute basis using  $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(b) Photolysis of  $\text{Cl}_2$  in presence of  $\text{CH}_2\text{F}_2$  and  $\text{CH}_4$  in 920 mbar air or  $\text{N}_2$  bath gas. The value obtained,  $k/\text{CH}_2\text{F}_2/k(\text{CH}_4) = 0.32 \pm 0.02$  was placed on an absolute value using  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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## Preferred Values

$k = 5.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 7.0 \times 10^{-12} \exp(-1470/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 280–370 K.

## Reliability

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

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

## Comments on Preferred Values

10 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

IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>, 2007.

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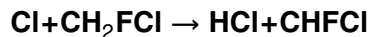
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$1.2 \times 10^{-11} \exp(-1230/T)$	273-368	Tschuikow-Roux et al., 1988	RR (a)
$1.9 \times 10^{-13}$	298		
$(1.10 \pm 0.25) \times 10^{-13}$	298	Tuazon et al., 1992	RR (b)

## 5 Comments

(a) Cl atoms were generated by the photolysis of  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 9.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

10 (b) Cl atoms were generated by photolysis of  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

## Preferred Values

15  $k = 1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 7.0 \times 10^{-12} \exp(-1230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270–16618

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370 K.

### **Reliability**

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

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

### 5 **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**

IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>, 2007.

10 Tschuikow-Roux, E., Faraji, F., Paddison, S., Niedzielski, J., and Miyokawa, K.: J. Phys. Chem., 92, 1488, 1988.

Tuazon, E. C., Atkinson, R., and Corchnoy, S. B.: Int. J. Chem. Kinet., 24, 639, 1992.

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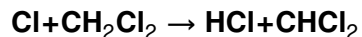
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$$\Delta H^\circ = -19.9 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.5 \pm 0.5) \times 10^{-13}$	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
$6.4 \times 10^{-13}$	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		
<i>Relative Rate Coefficients</i>			
$(3.65 \pm 0.39) \times 10^{-13}$	298	Niki et al., 1980	RR (a)
$1.9 \times 10^{-11} \exp(-1190/T)$	273–368	Tschuikow-Roux et al., 1988	RR (b)
$3.5 \times 10^{-13}$	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)
$3.2 \times 10^{-13}$			

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## Comments

- (a) Relative to Cl+CH<sub>3</sub>Cl. Cl atoms were generated by the photolysis of Cl<sub>2</sub> in the presence of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>Cl in air at 930 mbar and the concentrations of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>4</sub> measured by FTIR. The measured rate coefficient ratio of  $k(\text{Cl}+\text{CH}_2\text{Cl}_2)/k(\text{Cl}+\text{CH}_3\text{Cl}) = (0.76 \pm 0.08)$  was placed on an absolute basis using  $k(\text{Cl}+\text{CH}_3\text{Cl}) = 4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).
- (b) Cl atoms were generated by the photolysis of Cl<sub>2</sub> at 424 nm, and the concentrations of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>Cl measured by GC. The measured rate coefficient ratio of  $k(\text{Cl}+\text{CH}_2\text{Cl}_2)/k(\text{Cl}+\text{CH}_4) = (2.81 \pm 0.02) \exp[-(49 \pm 2)/T]$  is placed on an absolute basis by using the rate coefficient of  $k(\text{Cl}+\text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).
- (c) Cl atoms were generated from the photolysis of Cl<sub>2</sub> in Cl<sub>2</sub>-CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>4</sub> mixtures at atmospheric pressure of N<sub>2</sub>, air or Ar. The concentrations of CH<sub>3</sub>Cl and CH<sub>4</sub> were monitored by GC and a rate coefficient ratio  $k(\text{Cl}+\text{CH}_2\text{Cl}_2)/k(\text{Cl}+\text{CH}_4) = 3.45 \pm 0.18$  was determined. This was placed on an absolute basis by use of  $k(\text{Cl}+\text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).
- (d) Cl atoms were generated from the photolysis of Cl<sub>2</sub> in Cl<sub>2</sub>-CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>4</sub> in air at 930 mbar total pressure. The relative removal rates of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>4</sub> were measured by FTIR. A rate coefficient ratio  $k(\text{Cl}+\text{CH}_2\text{Cl}_2)/k(\text{Cl}+\text{CH}_4) = 3.51 \pm 0.14$  was obtained and placed on an absolute basis by use of  $k(\text{Cl}+\text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).
- (e) Cl atoms were generated from the photolysis of Cl<sub>2</sub> in Cl<sub>2</sub>-CH<sub>3</sub>Cl-CH<sub>4</sub> mixtures at 930 mbar total pressure of O<sub>2</sub>-N<sub>2</sub>. The concentrations of CH<sub>3</sub>Cl and CH<sub>4</sub> were monitored by FTIR absorption spectroscopy and a temperature dependent rate coefficient ratio  $k(\text{Cl}+\text{CH}_2\text{Cl}_2)/k(\text{Cl}+\text{CH}_4)$  determined. This was placed on an

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absolute basis by use of  $k(\text{Cl}+\text{CH}_4)=6.6\times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation). The results were consistent with those obtained using  $\text{CH}_3\text{Br}$  as reference reactant.

### Preferred Values

- 5  $k=3.4\times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.  
 $k=5.9\times 10^{-12} \exp(-850/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220–400 K.

### Reliability

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

### 10 *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  $(3.4\pm 0.3)\times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Note, that for reaction with  $\text{CH}_4$ , 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  $\approx 400 \text{ K}$ . 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,

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hence use of the 3-parameter fit of Bryukov et al. (2002) to cover temperatures up to 800 K.

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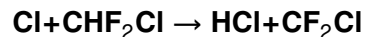
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$$\Delta H^\circ = -9.0 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.7 \pm 0.2) \times 10^{-15}$	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		
<i>Relative Rate Coefficients</i>			
$(2.0 \pm 0.4) \times 10^{-15}$	298	Tuazon, et al., 1992	RR (a)

**Comments**

(a) Cl atoms were generated by photolysis of  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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## Preferred Values

$k = 1.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 5.9 \times 10^{-12} \exp(-2430/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290–430 K.

### 5 **Reliability**

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

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

### **Comments on Preferred Values**

10 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 15 298 K.

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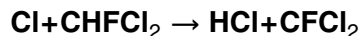
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$$\Delta H^\circ = -17.8 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.2 \times 10^{-12} \exp[-(1675 \pm 60)/T]$ $(1.9 \pm 0.3) \times 10^{-14}$	298–430 296	Talhaoui et al., 1996	DF-MS
<i>Relative Rate Coefficients</i>			
$(1.0 \pm 0.2) \times 10^{-14}$	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  $\text{Cl}_2\text{-CHFCI}_2\text{-O}_2\text{-NO-NO}_2\text{-N}_2$  mixtures. The measured rate coefficient ratio is placed on absolute basis by use of a rate coefficient of  $k(\text{Cl} + \text{NO} + \text{M}) = 1.0 \times 10^{-31} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

(a) Cl atoms were generated by the photolysis of  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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## Preferred Values

$k=2.0\times 10^{-14}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

$k=5.5\times 10^{-12}\exp(-1675/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 290–430 K.

### 5 **Reliability**

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

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

### **Comments on Preferred Values**

10 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.

### 15 **References**

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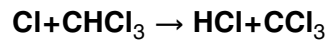
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## IV.A2.97



$$\Delta H^\circ = -39.2 \text{ kJ mol}^{-1}$$

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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.45 \times 10^{-11} \exp[-(1379 \pm 44)/T]$	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		
<i>Relative Rate Coefficients</i>			
$1.9 \times 10^{-12} \exp(-980/T)$	286–593	Knox, 1962	RR (b,c)
$6.9 \times 10^{-14}$	298		
$7.8 \times 10^{-12} \exp(-1350/T)$	240–593	Knox, 1962	RR (b,d)
$8.2 \times 10^{-14}$	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)
$1.15 \times 10^{-13}$	298		

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## Comments

- (a) Very low pressure reactor with chemiluminescence and mass spectrometric detection. The reaction of Cl with  $\text{CHCl}_3$  was studied as part of a complex chemical system.
- (b) Cl atoms were generated by photolysis of  $\text{Cl}_2$  in  $\text{Cl}_2$ - $\text{CHCl}_3$ - $\text{CH}_4$  or  $\text{Cl}_2$ - $\text{CHCl}_3$ - $\text{CH}_3\text{Cl}$  mixtures. Organic reactants and products monitored by GC.
- (c) Rate coefficient ratio of  $k(\text{Cl}+\text{CHCl}_3)/k(\text{Cl}+\text{CH}_4)=0.286 \exp(259/T)$  was obtained and placed on an absolute basis by use of  $k(\text{Cl}+\text{CH}_4)=6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).
- (d) Rate coefficient ratio of  $k(\text{Cl}+\text{CHCl}_3)/k(\text{Cl}+\text{CH}_3\text{Cl})=0.26 \exp(-133/T)$  obtained, and placed on an absolute basis by use of  $k(\text{Cl}+\text{CH}_3\text{Cl})=3.0 \times 10^{-11} \exp(-1220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).
- (e) Cl atoms were generated from the photolysis of  $\text{Cl}_2$  in  $\text{Cl}_2$ - $\text{CHCl}_3$ - $\text{CH}_4$  mixtures at atmospheric pressure of  $\text{N}_2$ , air or Ar. The concentrations of  $\text{CHCl}_3$  and  $\text{CH}_4$  were monitored by GC and a rate coefficient ratio  $k(\text{Cl}+\text{CHCl}_3)/k(\text{Cl}+\text{CH}_4)=1.13 \pm 0.07$  was determined. This was placed on an absolute basis by use of  $k(\text{Cl}+\text{CH}_4)=1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).
- (f) Cl atoms were generated by photolysis of  $\text{Cl}_2$  in  $\text{Cl}_2$ - $\text{CHCl}_3$ - $\text{CH}_4$  or  $\text{Cl}_2$ - $\text{CHCl}_3$ - $\text{CH}_3\text{Cl}$  mixtures in an air or  $\text{N}_2$  bath gas at 1023 mbar total pressure and 298 K. Rate coefficient ratios  $k(\text{Cl}+\text{CHCl}_3)/k(\text{Cl}+\text{CH}_4)$  and  $k(\text{Cl}+\text{CHCl}_3)/k(\text{Cl}+\text{CH}_3\text{Cl})$  were placed on an absolute basis by use of  $k(\text{Cl}+\text{CH}_4)=1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{Cl}+\text{CH}_3\text{Cl})=4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation). The value presented in the table is the average of experiments using both  $\text{CH}_4$  and  $\text{CH}_3\text{Cl}$  as reference reactants.

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(g) Cl atoms were generated from the photolysis of Cl<sub>2</sub> in Cl<sub>2</sub>-CHCl<sub>3</sub>-CH<sub>4</sub> mixtures at 930 mbar total pressure of air. The relative removal rates of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>4</sub> were measured by FTIR. A rate coefficient ratio  $k(\text{Cl}+\text{CHCl}_3)/k(\text{Cl}+\text{CH}_4)=1.1\pm 0.1$  was obtained and placed on an absolute basis by use of  $k(\text{Cl}+\text{CH}_4)=1.0\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation).

(h) Cl atoms were generated from the photolysis of Cl<sub>2</sub> in Cl<sub>2</sub>-CHCl<sub>3</sub>-CH<sub>4</sub> mixtures at 930 mbar total pressure of O<sub>2</sub>-N<sub>2</sub>. The concentrations of CHCl<sub>3</sub> and CH<sub>4</sub> were monitored by FTIR absorption spectroscopy and a temperature dependent rate coefficient ratio  $k(\text{Cl}+\text{CHCl}_3)/k(\text{Cl}+\text{CH}_4)$  determined. This was placed on an absolute basis by use of  $k(\text{Cl}+\text{CH}_4)=6.6\times 10^{-12}\text{ exp}(-1240/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation). The results were consistent with those obtained using CH<sub>3</sub>Br as reference reactant

### Preferred Values

$k=1.1\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

$k=2.4\times 10^{-12}\text{ exp}(-920/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 220–500 K.

### Reliability

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

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

### 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

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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  $220\text{ K} < T < 500\text{ K}$  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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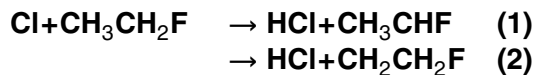
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$$\Delta H^\circ(1) = -9.6 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -5.3 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.8 \pm 0.5) \times 10^{-12}$	298	Hitsuda et al., 2001	PLP-LIF (a)
<i>Relative Rate Coefficients</i>			
$k_1 = 1.0 \times 10^{-11} \exp(-130/T)$	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  $\text{Cl}(^2\text{P}_{3/2})$  and  $\text{Cl}(^2\text{P}_{1/2})$  detected by VUV-LIF.

10 (b) Cl atoms were generated by the photolysis of  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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## Preferred Values

$k_1 = 6.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_1 = 1.0 \times 10^{-11} \exp(-130/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 280–370 K.

5  $k_2 = 7.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_2 = 8.3 \times 10^{-12} \exp(-720/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 280–370 K.

## Reliability

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

10  $\Delta (E_1/R) = \Delta (E_2/R) = \pm 500 \text{ K}$ .

## 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.

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15 Hitsuda, K., Takahashi, K., Matsumi, Y., and Wallington, T. J.: J. Phys. Chem. A, 105, 5131, 2001.

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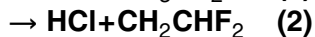
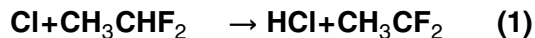
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## IV.A2.99



$$\Delta H^\circ(1) = -4.9 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -11.1 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$k_1 = 7.0 \times 10^{-12} \exp(-965/T)$	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  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{C}_2\text{H}_6) = 8.3 \times 10^{-11} \exp(-100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(b) Cl atoms were generated by the photolysis of  $\text{Cl}_2$ . 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  $k(\text{Cl}+\text{CH}_4)=1.0\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

$k_1=2.5\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

5  $k_1=6.3\times 10^{-12}\text{ exp}(-965/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 280–360 K.

$k_2=2.3\times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

$k_2=7.0\times 10^{-12}\text{ exp}(-2400/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 280–360 K.

### 10 *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*

15 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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Tuazon, E. C., Atkinson, R., and Corchnoy, S. B: Int. J. Chem. Kinet., 24, 639, 1992.

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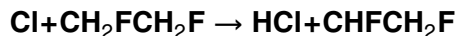
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$$\Delta H^\circ = -4.6 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.8 \times 10^{-11} \exp[-(1065)/T]$	280–360	Yano and Tschuikow-Roux, 1986	RR (a)
$7.8 \times 10^{-13}$	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  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{C}_2\text{H}_6) = 8.1 \times 10^{-11} \exp(-100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(b) Cl atoms were generated by the photolysis of  $\text{Cl}_2$  in presence of  $\text{CH}_2\text{FCH}_2\text{F}-\text{CH}_4$  in air at 930 mbar total pressure. Loss of reactants was monitored by FTIR. The measured rate coefficient ratio  $k(\text{Cl} + \text{CH}_2\text{FCH}_2\text{F})/k(\text{Cl} + \text{CH}_4) = (6.60 \pm 0.16)$  was placed on an absolute basis by use of a rate coefficient of  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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(c) Cl atoms were generated by the photolysis of Cl<sub>2</sub> in presence of CH<sub>2</sub>FCH<sub>2</sub>F-CH<sub>3</sub>Cl mixtures in air at 930 mbar total pressure. Loss of reactants was monitored by FTIR. The measured rate coefficient ratio  $k(\text{Cl}+\text{CH}_2\text{FCH}_2\text{F})/k(\text{Cl}+\text{CH}_3\text{Cl})=(1.36\pm 0.07)$  was placed on an absolute basis by use of a rate coefficient of  $k(\text{Cl}+\text{CH}_3\text{Cl})=4.8\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

$k=7.0\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

$k=2.5\times 10^{-11}\exp(-1065/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 280–360 K.

### Reliability

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

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

### 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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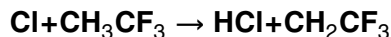
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$$\Delta H^\circ = 18.0 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$< 1 \times 10^{-14}$	298	Hitsuda et al., 2001	PLP-LIF (a)
<i>Relative Rate Coefficients</i>			
$6.9 \times 10^{-12} \exp(-3720/T)$	281–368	Tschuikow-Roux et al., 1985	RR (b)
$2.6 \times 10^{-17}$	298		

**Comments**

(a) Laser photolysis of HCl at 193 nm as Cl atom source. Both  $\text{Cl}(^2\text{P}_{3/2})$  and  $\text{Cl}(^2\text{P}_{1/2})$  detected by VUV-LIF.

10 (b) Cl atoms were generated by the photolysis of  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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## Preferred Values

$k = 2.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 6.9 \times 10^{-12} \exp(-3720/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 280–370 K.

### 5 *Reliability*

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

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

### *Comments on Preferred Values*

10 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.

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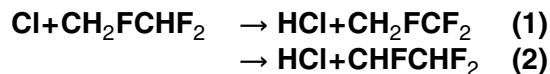
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## IV.A2.102



$$\Delta H^\circ(1) = 2.2 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = 0.0 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$k_1 = 3.3 \times 10^{-12} \exp(-1450/T)$	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  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

$$k_1 = 2.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_1 = 3.3 \times 10^{-12} \exp(-1450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 280\text{--}16644$$

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370 K.

$k_2 = 2.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_2 = 4.6 \times 10^{-12} \exp(-1560/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 280–370 K.

### 5 **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**

10 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.

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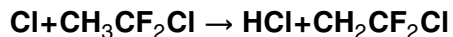
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.6 \pm 2.0) \times 10^{-16}$	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		
<i>Relative Rate Coefficients</i>			
$(3.90 \pm 0.52) \times 10^{-16}$	295	Wallington and Hurley, 1992	RR (a)
$(3.7 \pm 0.8) \times 10^{-16}$	298	Tuazon et al., 1992	RR (a)

## 5 Comments

(a) Cl atoms were generated by the photolysis of  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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## Preferred Values

$k=4.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k=1.4 \times 10^{-12} \exp(-2420/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 296–440 K.

### 5 **Reliability**

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

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

### **Comments on Preferred Values**

10 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.

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Talhaoui, A., Devolder, L. P., Meriaux, B., Sawerysyn, J.-P., Rayez, M.-T., and Rayez, J.-C.: J. Phys. Chem., 100, 13531, 1996.  
20 Tuazon, E. C., Atkinson, R. and Corchnoy, S. B.: Int. J. Chem. Kinet., 24, 639, 1992.  
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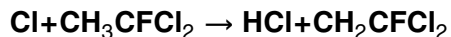
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.1 \pm 0.2) \times 10^{-15}$	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		
<i>Relative Rate Coefficients</i>			
$(2.0 \pm 0.2) \times 10^{-15}$	295	Wallington and Hurley, 1992	RR (a)
$(2.4 \pm 0.5) \times 10^{-15}$	298	Tuazon et al., 1992	RR (a)

## 5 Comments

(a) Cl atoms were generated by the photolysis of  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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## Preferred Values

$k=2.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k=1.7 \times 10^{-12} \exp(-2000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290–380 K.

### 5 **Reliability**

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

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

### **Comments on Preferred Values**

10 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).

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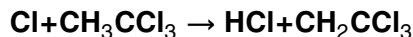
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$< 2.40 \times 10^{-14}$	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		
<i>Relative Rate Coefficients</i>			
$(9.9 \pm 2.0) \times 10^{-15}$	296	Platz et al., 1995	RR (a)

5 **Comments**

(a) Photolysis of  $\text{Cl}_2\text{-CH}_3\text{CCl}_3\text{-CD}_4$  mixtures in air or  $\text{N}_2$  at 930 mbar total pressure, with the loss of reactants monitored by FTIR. A value of  $k(\text{Cl} + \text{CH}_3\text{CCl}_3)/k(\text{Cl} + \text{CD}_4) = (1.62 \pm 0.05)$  was obtained and placed on an absolute basis using  $k(\text{Cl} + \text{CD}_4) = 6.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Wallington and Hurley, 1992).

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## Preferred Values

$k = 7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 2.8 \times 10^{-12} \exp(-1790/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290–420 K.

### 5 **Reliability**

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

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

### **Comments on Preferred Values**

10 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).

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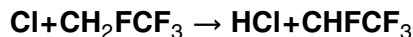
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$$\Delta H^\circ = 1.8 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.6 \pm 0.3) \times 10^{-15}$	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		
<i>Relative Rate Coefficients</i>			
$(1.38 \pm 0.18) \times 10^{-15}$	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  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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## Preferred Values

$k = 1.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 3.4 \times 10^{-12} \exp(-2300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 299–430 K.

## 5 Reliability

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

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

## Comments on Preferred Values

10 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.

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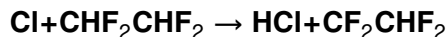
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$$\Delta H^\circ = 6.5 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$8.9 \times 10^{-12} \exp(-2444/T)$	280–360	Yano and Tschuikow-Roux, 1986	RR (a)
$2.4 \times 10^{-15}$	298		
$1.9 \times 10^{-15}$	298	Nielsen et al., 1992	RR (b)

**Comments**

(a) Cl atoms were generated by the photolysis of  $\text{Cl}_2$ . Product yield ratios were measured by GC. The measured rate coefficient ratio was placed on an absolute basis by use of  $k(\text{Cl} + \text{C}_2\text{H}_6) = 8.3 \times 10^{-11} \exp(-100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(b) Cl atoms were generated by the photolysis of  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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## Preferred Values

$k = 2.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 7.9 \times 10^{-12} \exp(-2440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 280–360 K.

### 5 **Reliability**

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

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

### **Comments on Preferred Values**

10 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.

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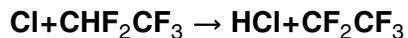
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$$\Delta H^\circ = 10.7 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(2.4 \pm 0.5) \times 10^{-16}$	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  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(b) Cl atoms were generated by the photolysis of  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_3\text{CF}_2\text{Cl}) = 4.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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## Preferred Values

$k=2.5\times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

## Reliability

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

## 5 *Comments on Preferred Values*

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.

## 10 **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.

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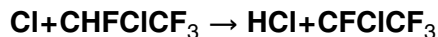
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**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.16 \times 10^{-12} \exp[-(1800 \pm 150)/T]$	276–376	Warren and Ravishankara, 1993	PLP-RF
$(2.62 \pm 0.50) \times 10^{-15}$	298		
<i>Relative Rate Coefficients</i>			
$(2.7 \pm 0.6) \times 10^{-15}$	298	Tuazon et al. 1992	RR (a)

5 **Comments**

(a) Cl atoms were generated by the photolysis of  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

10 **Preferred Values**

$k = 2.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.1 \times 10^{-12} \exp(-1800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270–380 K.

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## Reliability

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

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

## Comments on Preferred Values

- 5 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

- 10 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.

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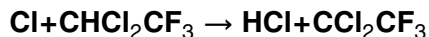
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**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.94 \times 10^{-12} \exp[-(1740 \pm 100)/T]$	276–382	Warren and Ravishankara, 1993	PLP-RF
$(1.15 \pm 0.30) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$(1.22 \pm 0.18) \times 10^{-14}$	295	Wallington and Hurley, 1992	RR (a)
$(1.4 \pm 0.3) \times 10^{-14}$	298	Tuazon et al. 1992	RR (a)

5 **Comments**

(a) Cl atoms were generated by the photolysis of  $\text{Cl}_2$ . 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  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

10 **Preferred Values**

$k = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 4.4 \times 10^{-12} \exp(-1740/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270–380 K.

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## Reliability

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

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

## Comments on Preferred Values

- 5 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.

## 10 References

IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>, 2007.

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Warren, R. F. and Ravishankara, A. R.: Int. J. Chem. Kinet., 25, 833, 1993.

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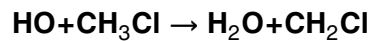
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$$\Delta H^\circ = -79.8 \text{ kJ mol}^{-1}$$

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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.6 \pm 0.8) \times 10^{-14}$	296 $\pm$ 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		
<i>Relative Rate Coefficients</i>			
$7.8 \times 10^{-14}$	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)
$3.53 \times 10^{-14}$	298		

## Comments

(a) These data supersede the earlier data from this group (Taylor et al., 1989).

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(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<sub>3</sub>Cl on NO formation and a rate coefficient for the reaction of HO radicals with CH<sub>4</sub> of  $6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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<sub>3</sub> in the presence of water vapor. The concentrations of CH<sub>3</sub>Cl and CH<sub>3</sub>CHF<sub>2</sub> were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CH}_3\text{Cl})/k(\text{HO}+\text{CH}_3\text{CHF}_2)=(1.91 \pm 0.45) \exp[-(195 \pm 74)/T]$  is placed on an absolute base by using a rate coefficient of  $k(\text{HO}+\text{CH}_3\text{CHF}_2)=2.80 \times 10^{-18} T^2 \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

**Preferred Values**

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

$k=2.1 \times 10^{-12} \exp(-1210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220–300 K.

**Reliability**

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

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

## 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  $k = 4.34 \times 10^{-18} T^2 \exp(-700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 224–398 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 255 K and is obtained from the three parameter equation with  $A = C e^2 T^2$  and  $B = D + 2T$ . 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  $k(\text{HO} + {}^{12}\text{CH}_3\text{Cl})/k(\text{HO} + {}^{13}\text{CH}_3\text{Cl}) = 1.059 \pm 0.008$  at  $298 \pm 2 \text{ K}$ , and the deuterium isotope effect for the reaction of HO radicals with  $\text{CD}_3\text{Cl}$ , of  $k(\text{HO} + \text{CH}_3\text{Cl})/k(\text{HO} + \text{CD}_3\text{Cl}) = 3.9 \pm 0.4$  at  $298 \pm 2 \text{ K}$ .

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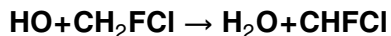
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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.7 \pm 0.6) \times 10^{-14}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$2.84 \times 10^{-12} \exp[-(1259 \pm 50)/T]$	245–375	Watson et al., 1977	FP-RF
$(4.21 \pm 0.41) \times 10^{-14}$	298		
$3.1 \times 10^{-12} \exp[-(1320 \pm 100)/T]$	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
$1.57 \times 10^{-19} T^{2.41} \exp[-(307 \pm 382)/T]$	250–486	Jeong and Kaufman, 1982;	DF-RF
$(4.94 \pm 0.30) \times 10^{-14}$	295	Jeong et al., 1984	
<i>Relative Rate Coefficients</i>			
$1.46 \times 10^{-12} \exp[-(1076 \pm 24)/T]$	293–371	DeMore, 1996	RR (a)
$3.95 \times 10^{-14}$	298		

## 5 Comments

(a) HO radicals were generated by the photolysis of  $\text{O}_3$  at 254 nm in the presence of  $\text{H}_2\text{O}$ , and  $\text{CH}_2\text{Cl}_2$  was used as the reference compound.  $\text{CH}_2\text{FCI}$  and  $\text{CH}_2\text{Cl}_2$  were monitored by FTIR spectroscopy, and a rate coefficient ratio of  $k(\text{HO} + \text{CH}_2\text{FCI})/k(\text{HO} + \text{CH}_2\text{Cl}_2) = 0.81 \exp[-(216 \pm 24)/T]$  was determined. This

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rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO}+\text{CH}_2\text{Cl}_2)=1.8\times 10^{-12} \exp(-860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

- 5  $k=3.9\times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.  
 $k=1.6\times 10^{-12} \exp(-1105/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240–300 K.

### Reliability

- $\Delta \log k=\pm 0.1$  at 298 K.  
10  $\Delta (E/R)=\pm 200$  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  
15 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  $k=3.03\times 10^{-18} T^2 \exp(-574/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the  
20 temperature range 245–375 K. The preferred Arrhenius expression,  $k=A \exp(-B/T)$ ,

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is centered at 265 K and is obtained from the three parameter equation with  $A=Ce^2 T^2$  and  $B=D + 2T$ .

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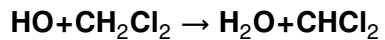
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$$\Delta H^\circ = -94.6 \text{ kJ mol}^{-1}$$

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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.55 \pm 0.34) \times 10^{-13}$	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		
<i>Relative Rate Coefficients</i>			
$9.5 \times 10^{-14}$	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)
$9.25 \times 10^{-14}$	298		
$1.96 \times 10^{-18} T^2 \exp[-(104 \pm 20)/T]$	298–368	Hsu and DeMore, 1994	RR (c,e)
$1.22 \times 10^{-13}$	298		

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## 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<sub>2</sub>Cl<sub>2</sub> on NO formation and a rate coefficient for the reaction of HO radicals with CH<sub>4</sub> of  $6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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<sub>3</sub> in the presence of water vapor. CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CHF<sub>2</sub> (or CH<sub>3</sub>CH<sub>2</sub>F) concentrations were measured by FTIR spectroscopy. The measured rate coefficient ratios of  $k(\text{HO} + \text{CH}_2\text{Cl}_2)/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (0.97 \pm 0.09) \exp[(294 \pm 29)/T]$  and  $k(\text{HO} + \text{CH}_2\text{Cl}_2)/k(\text{HO} + \text{CH}_3\text{CH}_2\text{F}) = (0.32 \pm 0.02) \exp[(171 \pm 20)/T]$  are placed on an absolute basis by using rate coefficients of  $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 2.80 \times 10^{-18} T^2 \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation) and  $k(\text{HO} + \text{CH}_3\text{CH}_2\text{F}) = 6.12 \times 10^{-18} T^2 \exp(-275/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).
- (d) Relative to HO+CH<sub>3</sub>CHF<sub>2</sub>.
- (e) Relative to HO+CH<sub>3</sub>CH<sub>2</sub>F<sub>2</sub>.

## Preferred Values

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

$k = 1.8 \times 10^{-12} \exp(-860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 210–400 K.

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## Reliability

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

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

## Comments on Preferred Values

5 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  $\text{CH}_2\text{Cl}_2$  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  $\text{HO} + \text{CH}_3\text{CHF}_2$  are  $\sim 5$ – $10\%$  lower than the preferred values and those relative to  $\text{HO} + \text{CH}_3\text{CH}_2\text{F}$  are  $\sim 15$ – $20\%$  higher than the preferred values over the temperature ranges 298–360 K and 298–368 K, respectively.

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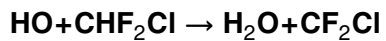
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$$\Delta H^\circ = -74.4 \text{ kJ mol}^{-1}$$

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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.21 \times 10^{-12} \exp[-(1636 \pm 151)/T]$ $(4.75 \pm 0.48) \times 10^{-15}$ $(3.4 \pm 0.7) \times 10^{-15}$	297–434 296.9 296 ± 2	Atkinson et al., 1976 Howard and Evenson, 1976	FP-RF DF-LMR
$9.25 \times 10^{-13} \exp[-(1575 \pm 71)/T]$ $(4.8 \pm 0.46) \times 10^{-15}$	250–350 298	Watson et al., 1977	FP-RF
$1.20 \times 10^{-12} \exp[-(1657 \pm 39)/T]$ $(4.25 \pm 0.28) \times 10^{-15}$	253–427 296	Chang and Kaufman, 1977	DF-RF
$2.1 \times 10^{-12} \exp[-(1780 \pm 150)/T]$ $(4.6 \pm 0.8) \times 10^{-15}$	263–373 293	Handwerk and Zellner, 1978	FP-RA
$9.5 \times 10^{-12} \exp[-(2300 \pm 200)/T]$ $(3.3 \pm 0.7) \times 10^{-15}$ $(4.58 \pm 0.59) \times 10^{-15}$	294–426 294 297	Clyne and Holt, 1979 Paraskevopoulos et al., 1981	DF-RF FP-RA
$5.03 \times 10^{-28} T^{5.11} \exp[-(252 \pm 780)/T]$ $(4.83 \pm 0.32) \times 10^{-15}$	293–492 293	Jeong and Kaufman, 1982; Jeong et al., 1984	DF-RF
$8.1 \times 10^{-13} \exp[-(1516 \pm 53)/T]$ $(4.9 \pm 0.45) \times 10^{-15}$	298–460 298	Orkin and Khamaganov, 1993	DF-EPR
$1.74 \times 10^{-12} \exp[-(1701 \pm 39)/T]$ $5.99 \times 10^{-15}$	302–382 302	Yujing et al., 1993	DF-RF

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.31 \times 10^{-22} T^{3.28} \exp[-(361 \pm 564)/T]$ $(4.65 \pm 0.66) \times 10^{-15}$	294-807 294	Fang et al., 1996	PLP-LIF
<i>Relative Rate Coefficients</i>			
$4.44 \times 10^{-21} T^{2.82} \exp[-(645 \pm 45)/T]$ $4.83 \times 10^{-15}$	298-366 298	Hsu and DeMore, 1995	RR (a)

## Comments

(a) HO radicals were generated by the UV photolysis of O<sub>3</sub> in the presence of water vapor. The concentrations of CHF<sub>2</sub>Cl and CH<sub>4</sub> were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CHF}_2\text{Cl})/k(\text{HO}+\text{CH}_4)=(0.24 \pm 0.03) \exp[(342 \pm 45)/T]$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+\text{CH}_4)=1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

## Preferred Values

$k=4.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.  
 $k=7.9 \times 10^{-13} \exp(-1530/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240–300 K.

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## Reliability

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

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

## Comments on Preferred Values

5 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 coeffi-  
cients of Hsu and DeMore (1995) agree well with these absolute rate coefficients. The  
10 absolute rate coefficients of Clyne and Holt (1979) exhibit a significantly higher tem-  
perature 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 Kauf-  
15 man (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 Kauf-  
20 man (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  $k = 1.52 \times 10^{-18} T^2 \exp(-$   
 $1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–807 K. The preferred  
Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 265 K and is obtained from the  
three parameter equation with  $A = Ce^2 T^2$  and  $B = D + 2T$ . The relative rate data of Hsu  
25 and DeMore (1995) agree to within 3% with the preferred values.

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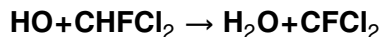
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$$\Delta H^\circ = -83.2 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.6 \pm 0.4) \times 10^{-14}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$1.75 \times 10^{-12} \exp[-(1253 \pm 151)/T]$	298–422	Perry et al., 1976	FP-RF
$(2.7 \pm 0.3) \times 10^{-14}$	298.4		
$1.87 \times 10^{-12} \exp[-(1245 \pm 26)/T]$	245–375	Watson et al., 1977	FP-RF
$(2.88 \pm 0.24) \times 10^{-14}$	298		
$1.16 \times 10^{-12} \exp[-(1073 \pm 40)/T]$	241–396	Chang and Kaufman, 1977	DF-RF
$(3.04 \pm 0.11) \times 10^{-14}$	296		
$4.8 \times 10^{-12} \exp[-(1400 \pm 100)/T]$	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
$1.97 \times 10^{-18} T^{1.94} \exp[-(382 \pm 413)/T]$	250–483	Jeong and Kaufman, 1982	DF-RF
$(3.37 \pm 0.22) \times 10^{-14}$	295	Jeong et al., 1984	
$1.53 \times 10^{-15} T^{1.11} \exp[-(1078 \pm 262)/T]$	295–810	Fang et al., 1996	PLP-LIF
$(2.48 \pm 0.67) \times 10^{-14}$	295		

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## Preferred Values

$k=2.9\times 10^{-14}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

$k=1.04\times 10^{-12}\exp(-1065/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 240–300 K.

## 5 Reliability

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

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

## Comments on Preferred Values

10 The 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  
15 Fang et al. (1996) have been fitted to the three parameter equation  $k=CT^2\exp(-D/T)$ , resulting in  $k=2.00\times 10^{-18}T^2\exp(-535/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 241–810 K. The preferred Arrhenius expression,  $k=A\exp(-B/T)$ , is centered at 265 K and is obtained from the three parameter equation with  $A=Ce^2T^2$  and  $B=D+2T$ .

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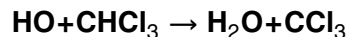
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$$\Delta H^\circ = -104.6 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.01 \pm 0.15) \times 10^{-13}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$4.69 \times 10^{-12} \exp[-(1134 \pm 108)/T]$	245–375	Davis et al., 1976	FP-RF
$(1.14 \pm 0.07) \times 10^{-13}$	298		
$6.91 \times 10^{-20} T^{2.65} \exp[-(262 \pm 398)/T]$	249–487	Jeong and Kaufman, 1982;	DF-RF
$(1.01 \pm 0.065) \times 10^{-13}$	298	Jeong et al., 1984	
$4.65 \times 10^{-17} T^{1.52} \exp[-(261 \pm 42)/T]$	295–775	Taylor et al., 1993	PLP-LIF (a)
$(1.12 \pm 0.10) \times 10^{-13}$	295		
<i>Relative Rate Coefficients</i>			
$1.53 \times 10^{-13}$	298	Cox et al., 1976	RR (b)
$1.46 \times 10^{-18} T^2 \exp[-(85 \pm 64)/T]$	288–357	Hsu and DeMore, 1994	RR (c)
$9.75 \times 10^{-14}$	298		

**Comments**

(a) These data supersede the earlier data from this group (Taylor et al., 1989).

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(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  $\text{CHCl}_3$  on NO formation and a rate coefficient for the reaction of HO radicals with  $\text{CH}_4$  of  $6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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  $\text{O}_3$  in the presence of water vapor. The concentrations of  $\text{CHCl}_3$  and  $\text{CH}_3\text{CHF}_2$  were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CHCl}_3)/k(\text{HO}+\text{CH}_3\text{CHF}_2)=(0.52 \pm 0.11) \exp[(495 \pm 64)/T]$  is placed on an absolute base by using a rate coefficient of  $k(\text{HO}+\text{CH}_3\text{CHF}_2)=2.80 \times 10^{-18} T^2 \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

$k=1.05 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k=1.8 \times 10^{-12} \exp(-850/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240–300 K.

### Reliability

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

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

### 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),

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Jeong and Kaufman (1982), Taylor et al. (1993) and Hsu and DeMore (1994) ranging from  $9.75 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  to  $1.14 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . 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  $< 288 \text{ K}$ , one by Davis et al. (1976) at  $245 \text{ K}$  and the other by Jeong and Kaufman (1982) at  $249 \text{ K}$ .

The  $298 \text{ K}$  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  $240\text{--}300 \text{ K}$  is obtained by averaging the Arrhenius activation energies centered at  $265 \text{ K}$ , 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  $B=D+2T$  (the Arrhenius activation energies being  $1134 \text{ K}$  for the Davis et al. (1976) study,  $964 \text{ K}$  for the Jeong and Kaufman (1982) study,  $664 \text{ K}$  for the Taylor et al. (1993) study and  $615 \text{ K}$  for the Hsu and DeMore (1994) study, all centered at  $265 \text{ K}$ ). The preferred Arrhenius expression, which should not be used outside of the temperature range  $240\text{--}300 \text{ K}$ , leads to rate coefficients at  $245 \text{ K}$  and  $249 \text{ K}$  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  $240\text{--}300 \text{ K}$  is equivalent to the three parameter equation  $k=3.47 \times 10^{-18} T^2 \exp(-320/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). Clearly, additional studies of this reaction covering the temperature range  $\sim 200\text{--}400 \text{ K}$  are needed.

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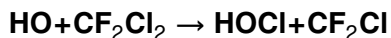
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$$\Delta H^\circ = 99.0 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<1 \times 10^{-15}$	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
<i>Relative Rate Coefficients</i>			
$<9 \times 10^{-17}$	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  $\text{CF}_2\text{Cl}_2$  on NO formation and a rate coefficient for the reaction of HO radicals with  $\text{CH}_4$  of  $6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC, current recommendation), the upper limit to the rate coefficient cited in the table is obtained.

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## Preferred Values

$k < 7 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k < 1 \times 10^{-12} \exp(-3540/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–480 K.

## Comments on Preferred Values

- 5 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  $\text{CF}_2\text{Cl}_2$ . The preferred upper limit Arrhenius expression is obtained from an assumed Arrhenius pre-exponential factor of  $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and the upper limit rate coefficient at 478 K measured by Chang and Kaufman (1977). The
- 10 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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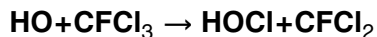
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$$\Delta H^\circ = 80.6 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<1 \times 10^{-15}$	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
<i>Relative Rate Coefficients</i>			
$<4 \times 10^{-17}$	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  $\text{CFCl}_3$  on NO formation and a rate coefficient for the reaction of HO radicals with  $\text{CH}_4$  of  $6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC, current recommendation), the upper limit to the rate coefficient cited in the table is obtained.

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## Preferred Values

$k < 5 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k < 1 \times 10^{-12} \exp(-3650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–480 K.

## Comments on Preferred Values

- 5 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  $\text{CFCl}_3$ . The preferred upper limit Arrhenius expression is obtained from an assumed Arrhenius pre-exponential factor of  $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and the upper limit at 480 K measured by Chang and Kaufman (1977). The resulting upper limit
- 10 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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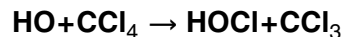
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$$\Delta H^\circ = 51.7 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<4 \times 10^{-15}$	296±2	Howard and Evenson, 1976	DF-LMR
$<1 \times 10^{-15}$	293	Clyne and Holt, 1979	DF-RF
<i>Relative Rate Coefficients</i>			
$<9 \times 10^{-17}$	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  $\text{CCl}_4$  on NO formation and a rate coefficient for the reaction of HO radicals with  $\text{CH}_4$  of  $6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC, current recommendation), the upper limit to the rate coefficient cited in the table is obtained.

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## Preferred Values

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

$k < 1 \times 10^{-12} \exp(-2260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range ~250–300 K.

### 5 *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<sub>4</sub>. 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<sub>4</sub> 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  $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

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HO+C<sub>2</sub>HCl<sub>3</sub> → products

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.0 \pm 0.4) \times 10^{-12}$	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		
$2.11 \times 10^{-12}$	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)
$1.66 \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(4.3 \pm 1.3) \times 10^{-12}$	305 ± 2	Winer et al., 1976	RR (b)
$(2.64 \pm 0.37) \times 10^{-12}$	296	Edney et al., 1986	RR (c)
$2.65 \times 10^{-12}$	300	Klöppfer et al., 1986	RR (d)

## 5 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–

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750 K, by the three parameter expression  $k=3.76 \times 10^{-21} T^{2.76} \exp(-1266.3 \pm 41.2/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

(b) HO radicals were generated by the photolysis of  $\text{NO}_x$ -organic-air mixtures at  $\sim 1$  bar of air. Trichloroethene and 2-methylpropene (the reference compound) were monitored by GC. The measured rate coefficient ratio  $k(\text{HO}+\text{trichloroethene})/k(\text{HO}+2\text{-methylpropene})=0.088 (\pm 30\%)$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO}+2\text{-methylpropene})=4.94 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 305 K (Atkinson, 1997).

(c) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO-NO}$ -air mixtures at  $\sim 1$  bar of air. Trichloroethene and n-butane (the reference compound) were monitored by GC. The measured rate coefficient ratio  $k(\text{HO}+\text{trichloroethene})/k(\text{HO}+\text{n-butane})$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO}+\text{n-butane})=2.33 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K (Atkinson, 2003).

(d) HO radicals were generated by the photolysis of  $\text{NO}_x$ -organic-air mixtures at  $\sim 1$  bar of air. Trichloroethene and toluene (the reference compound) were monitored by GC. The measured rate coefficient ratio  $k(\text{HO}+\text{trichloroethene})/k(\text{HO}+\text{toluene})$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO}+\text{toluene})=5.58 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K (Calvert et al., 2002).

### Preferred Values

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

$k=3.0 \times 10^{-13} \exp(565/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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

5 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)].  
10 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  $k = 6.06 \times 10^{-19} T^2 \exp(1084/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 234–650 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 260 K and is obtained from the three parameter equation with  $A = C e^2 T^2$  and  $B = D + 2T$ . 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  $B = -241 \pm 61$  K is in reasonable agreement with the value of  $B = -364$  K derived from the preferred three parameter expression centered at 360 K.  
20

25 The reaction proceeds by initial HO radical addition to form the HOCHCICCl<sub>2</sub> and HOCCl<sub>2</sub>CHCl radicals, which under atmospheric conditions lead to the formation of Cl atoms, HC(O)Cl, C(O)Cl<sub>2</sub> and other, as yet unidentified, products (Tuazon et al., 1988;

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HO+C<sub>2</sub>Cl<sub>4</sub> → products

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.70 \pm 0.34) \times 10^{-13}$	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		
<i>Relative Rate Coefficients</i>			
$(2.2 \pm 0.7) \times 10^{-12}$	305 ± 2	Winer et al., 1976	RR (b)

## 5 Comments

(a) Tichenor et al. (2000) also fit their data to an Arrhenius expression, obtaining  $k = 1.68 \times 10^{-12} \exp[-(764.2 \pm 79.1)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the same temperature range of 296.5–714 K.

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(b) HO radicals were generated by the photolysis of NO<sub>x</sub>-organic-air mixtures at ~1 bar of air. Tetrachloroethene and 2-methylpropene (the reference compound) were monitored by GC. The measured rate coefficient ratio  $k(\text{HO}+\text{tetrachloroethene})/k(\text{HO}+2\text{-methylpropene})=0.044$  ( $\pm 30\%$ ) is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO}+2\text{-methylpropene})=4.94\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 305 K (Atkinson, 1997).

### Preferred Values

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

$k=3.5\times 10^{-12}\exp(-920/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 290–420 K.

### Reliability

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

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

### 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, Kirchner et al. (1990),

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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  $\leq 220$  K are clearly needed.

The reaction proceeds by initial HO radical addition to form the HOCCl<sub>2</sub>CCl<sub>2</sub> radical, which under atmospheric conditions leads to the formation of Cl atoms, C(O)Cl<sub>2</sub> and other, as yet unidentified, products (Tuazon et al., 1988). The molar formation yield of C(O)Cl<sub>2</sub> 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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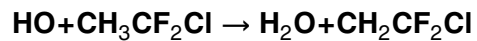
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.83 \pm 0.42) \times 10^{-15}$	296	Howard and Evenson, 1976	DF-LMR
$1.15 \times 10^{-12} \exp[-(1748 \pm 30)/T]$	273–375	Watson et al., 1977	FP-RF
$(3.22 \pm 0.48) \times 10^{-15}$	298		
$1.8 \times 10^{-12} \exp[-(1790 \pm 150)/T]$	293–373	Handwerk and Zellner, 1978	FP-RA
$(3.7 \pm 0.7) \times 10^{-15}$	293		
$3.3 \times 10^{-12} \exp[-(1800 \pm 300)/T]$	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
$9.8 \times 10^{-13} \exp[-(1660 \pm 200)/T]$	270–400	Liu et al., 1990	FP-RF
$(4.02 \pm 1.0) \times 10^{-15}$	298		
$2.6 \times 10^{-13} \exp[-(1230 \pm 250)/T]$	231–423	Brown et al., 1990	DF-RF
$(3.7 \pm 1.4) \times 10^{-15}$	303		
$1.14 \times 10^{-12} \exp[-(1750 \pm 75)/T]$	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
$2.05 \times 10^{-30} T^{6.01} \exp[(308 \pm 522)/T]$	295–808	Fang et al., 1997	PLP-LIF
$(3.77 \pm 0.43) \times 10^{-15}$	295		
<i>Relative Rate Coefficients</i>			
$3.5 \times 10^{-15}$	298	Cox et al., 1976	RR (b)

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## 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<sub>3</sub>CF<sub>2</sub>Cl on NO formation and a rate coefficient for the reaction of HO radicals with CH<sub>4</sub> of  $6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC, current recommendation), the rate coefficient cited in the table is obtained.

## Preferred Values

$k = 3.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.  
 $k = 8.5 \times 10^{-13} \exp(-1685/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220–300 K.

## Reliability

$\Delta \log k = \pm 0.10$  at 298 K.  
 $\Delta (E/R) = \pm 200 \text{ K}$ .

## Comments on Preferred Values

The rate coefficients obtained exhibit a large degree of scatter, especially at temperatures  $\leq 305 \text{ K}$ . 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

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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  $k = 1.77 \times 10^{-18} T^2 \exp(-1174/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 223–427 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 255 K and is obtained from the three parameter equation with  $A = C e^2 T^2$  and  $B = D + 2T$ .

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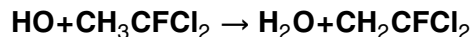
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.6 \times 10^{-13} \exp[-(1140 \pm 210)/T]$	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
<i>Relative Rate Coefficients</i>			
$9.07 \times 10^{-21} T^{2.82} \exp[-(798 \pm 105)/T]$	298–358	Huder and DeMore, 1993	RR (c,d)
$5.91 \times 10^{-15}$	298		
$1.78 \times 10^{-18} T^2 \exp[-(984 \pm 28)/T]$	298–358	Huder and DeMore, 1993	RR (c,e)
$5.85 \times 10^{-15}$	298		

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## 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<sub>3</sub>CFCl<sub>2</sub>. 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<sub>2</sub>O. 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<sub>2</sub>O-O<sub>3</sub> mixtures at 254 nm in H<sub>2</sub>O-O<sub>3</sub>-CH<sub>3</sub>CFCl<sub>2</sub>-CH<sub>4</sub> (or CH<sub>3</sub>CCl<sub>3</sub>)-Ar-O<sub>2</sub> mixtures. The concentrations of CH<sub>3</sub>CFCl<sub>2</sub> and CH<sub>4</sub> (or CH<sub>3</sub>CCl<sub>3</sub>) were measured by FTIR spectroscopy. The measured rate coefficient ratios of  $k(\text{HO} + \text{CH}_3\text{CFCl}_2)/k(\text{HO} + \text{CH}_4) = (0.49 \pm 0.16) \exp[(189 \pm 105)/T]$  and  $k(\text{HO} + \text{CH}_3\text{CFCl}_2)/k(\text{HO} + \text{CH}_3\text{CCl}_3) = (0.79 \pm 0.07) \exp[-(74 \pm 28)/T]$  are placed on an absolute basis by use of rate coefficients of  $k(\text{HO} + \text{CH}_4) = 1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation) and  $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(d) Relative to  $k(\text{HO} + \text{CH}_4)$ .

(e) Relative to  $k(\text{HO} + \text{CH}_3\text{CCl}_3)$ .

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## Preferred Values

$k=5.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k=8.1 \times 10^{-13} \exp(-1470/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220–300 K.

### 5 **Reliability**

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

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

### **Comments on Preferred Values**

10 The 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  $\leq 298 \text{ K}$  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  
15 temperature ( $\leq 298 \text{ K}$ ) 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  
20 of Talukdar et al. (1991) and Liu et al. (1990) at temperatures  $\geq 330 \text{ K}$ .

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  $k=1.68 \times 10^{-18} T^2 \exp(-962/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over

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the temperature range 233–479 K. The preferred Arrhenius expression,  $k=A \exp(-B/T)$ , is centered at 255 K and is obtained from the three parameter equation with  $A=C e^2 T^2$  and  $B=D+2T$ . The rate coefficients of Huder and DeMore (1993) over the temperature range 298–358 K, obtained relative to the reactions of HO radicals with

5 CH<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub>, agree to within 6% with those calculated from the preferred three parameter expression.

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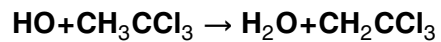
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.5 \pm 0.3) \times 10^{-14}$	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
$1.3 \times 10^{-14}$	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

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$2.57 \times 10^{-14}$	298	Cox et al., 1976	RR (b)
$(9.0 \pm 0.29) \times 10^{-15}$	298 $\pm$ 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  $k = 5.95 \times 10^{-20} T^{2.65} \exp[-(858 \pm 866)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (b) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO-NO}$ -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  $\text{CH}_3\text{CCl}_3$  on NO formation and a rate coefficient for the reaction of HO radicals with  $\text{CH}_4$  of  $6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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.  $\text{CH}_3\text{CCl}_3$  and  $\text{CH}_3\text{Cl}$  (the reference compound) were monitored during the experiments by GC. The measured rate coefficient ratio  $k(\text{HO} + \text{CH}_3\text{CCl}_3)/k(\text{HO} + \text{CH}_3\text{Cl})$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{CH}_3\text{Cl}) = 3.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC, current recommendation).
- (d) HO radicals were generated by the photolysis of  $\text{O}_3$  at 254 nm in  $\text{H}_2\text{O-O}_3\text{-CH}_3\text{CCl}_3\text{-CH}_4\text{-Ar-O}_2$  mixtures. The concentrations of  $\text{CH}_3\text{CCl}_3$  and  $\text{CH}_4$  were

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measured by FTIR spectroscopy. The measured rate coefficient ratios of  $k(\text{HO}+\text{CH}_3\text{CCl}_3)/k(\text{HO}+\text{CH}_4)=0.62 \exp(291/T)$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO}+\text{CH}_4)=1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

## 5 Preferred Values

$k=9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k=1.2 \times 10^{-12} \exp(-1440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240–300 K.

## Reliability

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

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

## 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  $\text{CH}_2=\text{CCl}_2$  impurities in the  $\text{CH}_3\text{CCl}_3$  samples used (Jeong and Kaufman, 1979; Kurylo et al., 1979) and/or the formation of  $\text{CH}_2=\text{CCl}_2$  from thermal decomposition of  $\text{CH}_3\text{CCl}_3$  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  $k=2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1}$

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$s^{-1}$  over the temperature range 243–379 K. The preferred Arrhenius expression,  $k=A \exp(-B/T)$ , is centered at 265 K and is obtained from the three parameter equation with  $A=C e^2 T^2$  and  $B=D+2T$ .

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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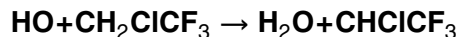
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.05 \pm 0.23) \times 10^{-14}$	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		

## 5 Preferred Values

$k = 1.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 5.6 \times 10^{-13} \exp(-1100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 260–380 K.

**Reliability**

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

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

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## 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 at 300 K, of  $B=1217$  K, in good agreement with the recommendation.

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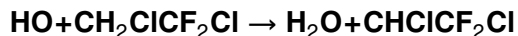
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.87 \times 10^{-12} \exp[-(1351 \pm 78)/T]$ $(1.9 \pm 0.2) \times 10^{-14}$	250–350 298	Watson et al., 1979	FP-RF (a)
$5.54 \times 10^{-26} T^{4.58} \exp[-(252 \pm 377)/T]$ $(2.42 \pm 0.16) \times 10^{-14}$	249–473 297	Jeong et al., 1984	DF-RF
$8.53 \times 10^{-19} T^{2.28} \exp[-(937 \pm 296)/T]$ $(1.84 \pm 0.07) \times 10^{-14}$	295–788 295	Fang et al., 1999	PLP-LIF

## 5 Comments

(a) The sample of  $\text{CH}_2\text{CICF}_2\text{Cl}$  used was shown by GC to contain  $\sim 0.045\%$  of  $\text{C}_2$  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  $\text{C}_2$  halogenated alkene impurities with HO radicals of  $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  independent of temperature, then the rate coefficient was estimated to be  $3 \times 10^{-12} \exp(-1578/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range of 250–350 K, with a rate coefficient at 298 K of  $1.67 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

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## Preferred Values

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

$k = 3.5 \times 10^{-12} \exp(-1585/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–350 K.

## 5 *Reliability*

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

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

## *Comments on Preferred Values*

10 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  $\text{CH}_2\text{ClCF}_2\text{Cl}$  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  
15 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  $k = 5.72 \times 10^{-18} T^2 \exp(-1006/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–788 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 290 K and is obtained from the three parameter equation with  $A = C e^2 T^2$  and  $B = D + 2T$ .

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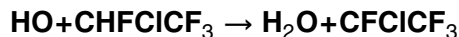
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.24 \pm 0.19) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
$6.13 \times 10^{-13} \exp[-(1244 \pm 90)/T]$	250–375	Watson et al., 1979	FP-RF
$(9.4 \pm 0.3) \times 10^{-15}$	301		
$4.45 \times 10^{-13} \exp[-(1150 \pm 60)/T]$	210–349	Gierczak et al., 1991	DF-LMR/FP-RF
$(9.44 \pm 0.75) \times 10^{-15}$	298		(a)
$7.72 \times 10^{-20} T^{2.35} \exp[-(458 \pm 30)/T]$	297–867	Yamada et al., 2000	PLP-LIF
$(1.08 \pm 0.16) \times 10^{-14}$	297		
<i>Relative Rate Coefficients</i>			
$6.48 \times 10^{-21} T^{2.82} \exp[-(620 \pm 40)/T]$	298–366	Hsu and DeMore, 1995	RR (b,c)
$7.68 \times 10^{-15}$	298		
$8.28 \times 10^{-19} T^2 \exp[-(674 \pm 52)/T]$	298–356	Hsu and DeMore, 1995	RR (b,d)
$7.66 \times 10^{-15}$	298		

## 5 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.

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(b) HO radicals were generated by the photolysis of H<sub>2</sub>O at 185 nm or from O<sub>3</sub>-H<sub>2</sub>O mixtures in the UV, in H<sub>2</sub>O (or H<sub>2</sub>O-O<sub>3</sub>)-CHFClCF<sub>3</sub>-CH<sub>4</sub> (or CHF<sub>2</sub>CHF<sub>2</sub>)-O<sub>2</sub>-N<sub>2</sub> mixtures. The concentrations of CHFClCF<sub>3</sub> and CH<sub>4</sub> (or CHF<sub>2</sub>CHF<sub>2</sub>) were measured by FTIR spectroscopy. The measured rate coefficient ratios of  $k(\text{HO}+\text{CHFClCF}_3)/k(\text{HO}+\text{CH}_4)=(0.35\pm 0.04) \exp[(367\pm 40)/T]$  and  $k(\text{HO}+\text{CHFClCF}_3)/k(\text{HO}+\text{CHF}_2\text{CHF}_2)=(0.46\pm 0.07) \exp[(300\pm 52)/T]$  are placed on an absolute basis by using rate coefficients of  $k(\text{HO}+\text{CH}_4)=1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation) and  $k(\text{HO}+\text{CHF}_2\text{CHF}_2)=1.80 \times 10^{-18} T^2 \exp(-974/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(c) Relative to  $k(\text{HO}+\text{CH}_4)$ .

(d) Relative to  $k(\text{HO}+\text{CHF}_2\text{CHF}_2)$ .

### Preferred Values

$k=8.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k=3.5 \times 10^{-13} \exp(-1105/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 210–300 K.

### Reliability

$\Delta \log k = \pm 0.20$  at 298 K.

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

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## 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  $\sim 1.6$ , 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  $\text{CH}_4$  and  $\text{CHF}_2\text{CHF}_2$  as reference compounds, are consistently lower than the absolute rate coefficients of Watson et al. (1979) and Gierczak et al. (1991), by  $\sim 15$ –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  $k = 7.47 \times 10^{-19} T^2 \exp(-606/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 210–425 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 250 K and is derived from the three parameter equation with  $A = C e^2 T^2$  and  $B = D + 2T$ . 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  $B = 1046 \text{ K}$ .

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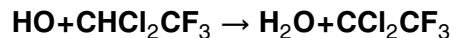
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.84 \pm 0.43) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
$1.24 \times 10^{-12} \exp[-(1056 \pm 70)/T]$	245–375	Watson et al., 1979	FP-RF (a)
$(3.6 \pm 0.4) \times 10^{-14}$	298		
$1.12 \times 10^{-12} \exp[-(1000 \pm 100)/T]$	293–429	Clyne and Holt, 1979	DF-RF
$(3.86 \pm 0.19) \times 10^{-14}$	293		
$1.1 \times 10^{-12} \exp[-(1040 \pm 140)/T]$	270–400	Liu et al., 1990	FP-RF
$(3.52 \pm 0.28) \times 10^{-14}$	298		
$1.18 \times 10^{-12} \exp[-(900 \pm 150)/T]$	232–426	Brown et al., 1990	DF-RF
$-(5.9 \pm 0.6) \times 10^{-14}$	303		
$6.5 \times 10^{-13} \exp[-(840 \pm 40)/T]$	213–322	Gierczak et al., 1991	DF-LMR/FP-RF (b)
$(3.69 \pm 0.37) \times 10^{-14}$	298		
$1.1 \times 10^{-12} \exp[-(940 \pm 200)/T]$	295–385	Nielsen, 1991	PR-RA
$(4.3 \pm 1.0) \times 10^{-14}$	295		
$2.20 \times 10^{-19} T^{2.88} \exp[-(226 \pm 51)/T]$	296–866	Yamada et al., 2000	PLP-LIF
$(3.67 \pm 0.24) \times 10^{-14}$	296.3		
<i>Relative Rate Coefficients</i>			
$7.84 \times 10^{-19} T^2 \exp[-(215 \pm 36)/T]$	298–359	Hsu and DeMore, 1995	RR (c)
$3.38 \times 10^{-14}$	298		

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## Comments

(a) The sample of  $\text{CHCl}_2\text{CF}_3$  used was shown by GC to contain 0.0227% of  $\text{C}_4\text{F}_5\text{HCl}_2$  and 0.0021% of  $\text{C}_4\text{F}_6\text{HCl}$ . 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  $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  independent of temperature, then the rate coefficient was estimated to be  $1.4 \times 10^{-12} \exp(-1102/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range of 245–375 K, with a rate coefficient at 298 K of  $3.49 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

(b) Rate coefficients were measured over the temperature range 213–380 K.

(c) HO radicals were generated by the photolysis of  $\text{H}_2\text{O}$  at 185 nm or  $\text{O}_3$  at 254 nm in the presence of  $\text{H}_2\text{O}$ , in  $\text{H}_2\text{O}$  (or  $\text{H}_2\text{O}-\text{O}_3$ )- $\text{CHCl}_2\text{CF}_3$ - $\text{CH}_3\text{CHF}_2$ - $\text{O}_2$ - $\text{N}_2$  mixtures. The concentrations of  $\text{CHCl}_2\text{CF}_3$  and  $\text{CH}_3\text{CHF}_2$  were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CHCl}_2\text{CF}_3)/k(\text{HO}+\text{CH}_3\text{CHF}_2)=(0.28 \pm 0.03) \exp[(365 \pm 36)/T]$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+\text{CH}_3\text{CHF}_2)=2.80 \times 10^{-18} T^2 \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

## Preferred Values

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

$k=6.6 \times 10^{-13} \exp(-870/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 210–300 K.

## Reliability

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

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

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## 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  $k = 1.42 \times 10^{-18} T^2 \exp(-370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 213–866 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 250 K and is obtained from the three parameter equation with  $A = C e^2 T^2$  and  $B = D + 2T$ .

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- Clyne, M. A. A. and Holt, P. M.: J. Chem. Soc. Faraday Trans. 2, 75, 582, 1979.
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Liu, R., Huie, R. E. and Kurylo, M. J.: J. Phys. Chem., 94, 3247, 1990.

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Yamada, T., Fang, T. D., Taylor, P. H., and Berry, R. J.: J. Phys. Chem. A, 104, 5013, 2000.

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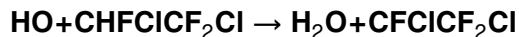
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**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$9.2 \times 10^{-13} \exp[-(1281 \pm 85)/T]$	298–460	Orkin and Khamaganov, 1993	DF-EPR
$(1.23 \pm 0.10) \times 10^{-14}$	298		

5 **Preferred Values**

$k = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 8.4 \times 10^{-13} \exp(-1255/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290–460 K.

**Reliability**10  $\Delta \log k = \pm 0.3$  at 298 K.

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

**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.

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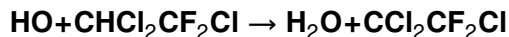
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.13 \times 10^{-12} \exp[-(918 \pm 52)/T]$ $(5.30 \pm 0.41) \times 10^{-14}$	298–460 298	Orkin and Khamaganov, 1993	DF-EPR
<i>Relative Rate Coefficients</i>			
$9.0 \times 10^{-13} \exp[-(868 \pm 32)/T]$ $4.87 \times 10^{-14}$	303-3-63 298*	DeMore, 1996	RR (a,b)
$1.36 \times 10^{-18} T^2 \exp[-(256 \pm 98)/T]$ $5.12 \times 10^{-14}$	313–371 298*	DeMore, 1996	RR (a,c)

## 5 Comments

(a) HO radicals were generated by the photolysis of  $\text{H}_2\text{O}$  at 185 nm or  $\text{O}_3$  at 254 nm in the presence of  $\text{H}_2\text{O}$ , in  $\text{H}_2\text{O}$  (or  $\text{H}_2\text{O}-\text{O}_3$ )- $\text{CHCl}_2\text{CF}_2\text{Cl}-\text{CH}_2\text{Cl}_2$  (or  $\text{CHCl}_2\text{CF}_3$ )- $\text{O}_2-\text{N}_2$  mixtures. The concentrations of  $\text{CHCl}_2\text{CF}_2\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  (or  $\text{CHCl}_2\text{CF}_3$ ) were measured by FTIR spectroscopy. The measured rate coefficient ratios of  $k(\text{HO} + \text{CHCl}_2\text{CF}_2\text{Cl})/k(\text{HO} + \text{CH}_2\text{Cl}_2) = (0.50 \pm 0.05) \exp[-(8 \pm 32)/T]$  and  $k(\text{HO} + \text{CHCl}_2\text{CF}_2\text{Cl})/k(\text{HO} + \text{CHCl}_2\text{CF}_3) = (0.96 \pm 0.28) \exp[(114 \pm 98)/T]$  are placed on an absolute basis by using rate coefficients of  $k(\text{HO} + \text{CH}_2\text{Cl}_2) = 1.8 \times 10^{-12} \exp(-860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation) and

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$k(\text{HO}+\text{CHCl}_2\text{CF}_3)=1.42 \times 10^{-18} T^2 \exp(-370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(b) Relative to  $k(\text{HO}+\text{CH}_2\text{Cl}_2)$ .

(c) Relative to  $k(\text{HO}+\text{CHCl}_2\text{CF}_3)$ .

## 5 Preferred Values

$k=5.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k=8.1 \times 10^{-13} \exp(-825/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270–340 K.

## Reliability

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

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

## 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  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_2\text{CF}_3$  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  $k=1.23 \times 10^{-18} T^2 \exp(-227/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 298–460 K. The preferred Arrhenius expression,  $k=A \exp(-B/T)$ , is centered at 300 K and is obtained from the three parameter equation with  $A=C e^2 T^2$  and  $B=D+2T$ .

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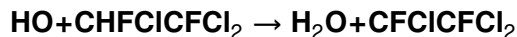
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$8.68 \times 10^{-19} T^2 \exp[-(463 \pm 42)/T]$	294–362	Hsu and DeMore, 1995	RR (a)
$1.63 \times 10^{-14}$	298		

## 5 Comments

(a) HO radicals were generated by the photolysis of  $\text{H}_2\text{O}$  at 185 nm or  $\text{O}_3$  at 254 nm in the presence of  $\text{H}_2\text{O}$ , in  $\text{H}_2\text{O}$  (or  $\text{H}_2\text{O}-\text{O}_3$ )- $\text{CHFClCFCl}_2$ - $\text{CH}_3\text{CHF}_2$ - $\text{O}_2$ - $\text{N}_2$  mixtures. The concentrations of  $\text{CHFClCFCl}_2$  and  $\text{CH}_3\text{CHF}_2$  were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CHFClCFCl}_2)/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (0.31 \pm 0.04) \exp[(117 \pm 42)/T]$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 2.80 \times 10^{-18} T^2 \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

## Preferred Values

$k = 1.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

15  $k = 5.8 \times 10^{-13} \exp(-1065/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270–340 K.

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## Reliability

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

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

## Comments on Preferred Values

- 5 The preferred values are based on 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 at 300 K and is derived from the cited three parameter expression,  $k = CT^2 \exp(-D/T)$ , with  $A = C e^2 T^2$  and  $B = D + 2T$ .

## References

- 10 Hsu, K.-J. and DeMore, W. B.: J. Phys. Chem., 99, 1235, 1995.  
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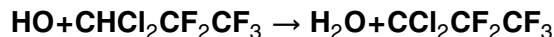
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.3 \times 10^{-13} \exp[-(550 \pm 750)/T]$	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		

## 5 Preferred Values

$k = 2.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.1 \times 10^{-12} \exp(-1130/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270–400 K.

**Reliability**

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

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

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## 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  $k = 1.56 \times 10^{-12} \exp(-1239/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , 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.

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- Nelson, D. D., Jr., Zahniser, M. S., and Kolb, C. E.: J. Phys. Chem., 96, 249, 1992.
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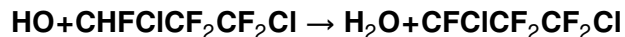
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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$6.75 \times 10^{-13} \exp[-(1300 \pm 180)/T]$ $(8.6 \pm 1.1) \times 10^{-15}$	298–400 298	Zhang et al., 1991	FP-RF
$3.9 \times 10^{-13} \exp[-(1120 \pm 125)/T]$ $(9.0 \pm 1.1) \times 10^{-15}$	295–374 295	Nelson et al., 1992	DF-LIF

### 5 Preferred Values

$k = 8.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 5.5 \times 10^{-13} \exp(-1230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290–400 K.

### Reliability

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

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

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## 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

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- Zhang, Z., Liu, R., Huie, R. E., and Kurylo, M. J.: Geophys. Res. Lett., 18, 5, 1991.

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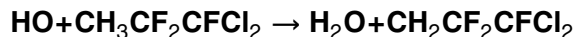
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**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$7.1 \times 10^{-13} \exp[-(1690 \pm 230)/T]$	295–367	Nelson et al., 1992	DF-LIF
$(2.1 \pm 0.2) \times 10^{-15}$	295		

5 **Preferred Values**

$k = 2.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 7.0 \times 10^{-13} \exp(-1690/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290–370 K.

**Reliability**

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

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

**Comments on Preferred Values**

The preferred values are based on the sole study of Nelson et al. (1992).

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Nelson, D. D., Jr., Zahniser, M. S., and Kolb, C. E.: J. Phys. Chem., 96, 249, 1992.

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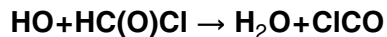
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**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$\leq 3.2 \times 10^{-13}$	299.2	Libuda et al., 1990	RR (a)

**Comments**

(a) HO radicals were generated by the thermal decomposition of  $\text{HO}_2\text{NO}_2$  after addition of NO to  $\text{HC(O)Cl}$ -*n*-butane- $\text{HO}_2\text{NO}_2$ - $\text{O}_2$ - $\text{N}_2$  mixtures at 800 mbar pressure. The concentrations of  $\text{HC(O)Cl}$  and *n*-butane were monitored by FTIR spectroscopy and GC, respectively. No decay of  $\text{HC(O)Cl}$  was observed, leading to the upper limit to the rate coefficient cited in the table.

**Preferred Values**

$k < 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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).

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Libuda, H. G., Zabel, F., Fink, E. H., and Becker, K. H.: J. Phys. Chem., 94, 5860, 1990.

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HO+CH<sub>3</sub>OCl → products

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.4 \times 10^{-12} \exp[-(360 \pm 100)/T]$ $(7.06 \pm 0.22) \times 10^{-13}$	250–341 294	Crowley et al., 1996	PLP-RF (a)

5 **Comments**

(a) HO radicals were generated from the pulsed laser photolysis of HNO<sub>3</sub> at 248 nm. CH<sub>3</sub>OCl-Ar samples were shown to be stable with respect to decomposition over long time periods (up to 3 months). Each CH<sub>3</sub>OCl-Ar sample used was analyzed for Cl<sub>2</sub> 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**

$k = 7.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 2.4 \times 10^{-12} \exp(-360/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–350 K.

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## Reliability

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

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

## Comments on Preferred Values

- 5 The preferred values are based on the sole study of this reaction by Crowley et al. (1996). The products have not been measured to date, but formation of  $\text{H}_2\text{O} + \text{CH}_2\text{OCl}$  and  $\text{HOCl} + \text{CH}_3\text{O}$  are possible.

## References

- 10 Crowley, J. N., Campuzano-Jost, P., and Moortgat, G. K., J. Phys. Chem. 100, 3601, (1996).

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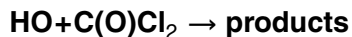
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**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$<1 \times 10^{-15}$	298±3	Nelson et al., 1990	RR (a)

**Comments**

(a) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO}$  in  $\text{CH}_3\text{ONO-NO-C(O)Cl}_2$ -reference compound-air mixtures at  $\sim 1$  bar pressure. The concentrations of  $\text{C(O)Cl}_2$  and the reference compound were monitored during the experiments by GC. No reaction of  $\text{C(O)Cl}_2$  was observed. However, no details concerning the reference compound used or the amount of reference compound reacted were given.

**Preferred Values**

$k < 5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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).

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Nelson, L., Shanahan, I., Sidebottom, H. W., Treacy, J., and Nielsen, O. J.: Int. J. Chem. Kinet., 22, 577, 1990.

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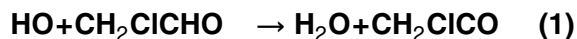
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### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.0 \pm 0.6) \times 10^{-12}$	298	Balestra-Garcia et al., 1992	PLP-RF
<i>Relative Rate Coefficients</i>			
$(3.2 \pm 0.2) \times 10^{-12}$	298 ± 2	Scollard et al., 1993	RR (a)

### 5 Comments

(a) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO}$  or  $\text{C}_2\text{H}_5\text{ONO}$  in  $\text{CH}_3\text{ONO}$  (or  $\text{C}_2\text{H}_5\text{ONO}$ )- $\text{NO}$ - $\text{CH}_2\text{ClCHO}$ - $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_3$ -air mixtures at  $987 \pm 13$  mbar pressure. The concentrations of  $\text{CH}_2\text{ClCHO}$  and 2-butanone were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CH}_2\text{ClCHO})/k(\text{HO} + 2\text{-butanone})$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + 2\text{-butanone}) = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC, current recommendation).

### Preferred Values

$k = 3.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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## 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 MacLeod, 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.

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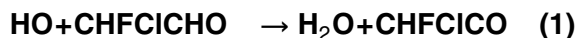
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## IV.A2.139

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.2 \pm 0.2) \times 10^{-12}$	298 $\pm$ 2	Scollard et al., 1993	PLP-RF
<i>Relative Rate Coefficients</i>			
$(1.9 \pm 0.3) \times 10^{-12}$	298 $\pm$ 2	Scollard et al., 1993	RR (a)

5 **Comments**

(a) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO}$  or  $\text{C}_2\text{H}_5\text{ONO}$  in  $\text{CH}_3\text{ONO}$  (or  $\text{C}_2\text{H}_5\text{ONO}$ )- $\text{CHFClCHO}$ -toluene-air mixtures at  $987 \pm 13$  mbar pressure. The concentrations of  $\text{CHFClCHO}$  and toluene were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CHFClCHO})/k(\text{HO} + \text{toluene})$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO} + \text{toluene}) = 5.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Calvert et al., 2002).

**Preferred Values**

$k = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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## 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.

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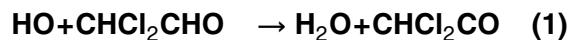
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### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.4 \pm 0.5) \times 10^{-12}$	298	Balestra-Garcia et al., 1992	PLP-RF
<i>Relative Rate Coefficients</i>			
$(2.4 \pm 0.1) \times 10^{-12}$	298 ± 2	Scollard et al., 1993	RR (a)

### 5 Comments

(a) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO}$  or  $\text{C}_2\text{H}_5\text{ONO}$  in  $\text{CH}_3\text{ONO}$  (or  $\text{C}_2\text{H}_5\text{ONO}$ )- $\text{NO}-\text{CHCl}_2\text{CHO}-\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_3$ -air mixtures at  $987 \pm 13$  mbar pressure. The concentrations of  $\text{CHCl}_2\text{CHO}$  and 2-butanone were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CHCl}_2\text{CHO})/k(\text{HO} + 2\text{-butanone})$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + 2\text{-butanone}) = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC, current recommendation).

### Preferred Values

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

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## Reliability

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

## Comments on Preferred Values

- 5 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

- 10 Balestra-Garcia, C., Le Bras, G., and MacLeod, 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.

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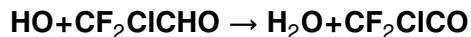
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.5 \pm 0.5) \times 10^{-13}$	298 $\pm$ 2	Scollard et al., 1993	PLP-RF
<i>Relative Rate Coefficients</i>			
$(6.9 \pm 0.5) \times 10^{-13}$	298 $\pm$ 2	Scollard et al., 1993	RR (a)

5 **Comments**

(a) HO radicals were generated by the photolysis of CH<sub>3</sub>ONO or C<sub>2</sub>H<sub>5</sub>ONO in CH<sub>3</sub>ONO (or C<sub>2</sub>H<sub>5</sub>ONO)-CF<sub>2</sub>CICHO-ethanol-air mixtures at 987 $\pm$ 13 mbar pressure. The concentrations of CF<sub>2</sub>CICHO and ethanol were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CF}_2\text{CICHO})/k(\text{HO} + \text{ethanol})$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO} + \text{ethanol}) = 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC, current recommendation).

**Preferred Values**

$k = 8.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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## 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.

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.

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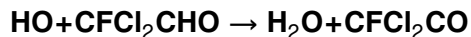
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.3 \pm 0.1) \times 10^{-12}$	298±2	Scollard et al., 1993	PLP-RF
<i>Relative Rate Coefficients</i>			
$(1.0 \pm 0.2) \times 10^{-12}$	298±2	Scollard et al., 1993	RR (a)

5 **Comments**

(a) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO}$  or  $\text{C}_2\text{H}_5\text{ONO}$  in  $\text{CH}_3\text{ONO}$  (or  $\text{C}_2\text{H}_5\text{ONO}$ )- $\text{CFCl}_2\text{CHO}$ -toluene-air mixtures at  $987 \pm 13$  mbar pressure. The concentrations of  $\text{CFCl}_2\text{CHO}$  and toluene were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CFCl}_2\text{CHO})/k(\text{HO} + \text{toluene})$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO} + \text{toluene}) = 5.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Calvert et al., 2002).

**Preferred Values**

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

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## Reliability

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

## Comments on Preferred Values

5 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.
- 10 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.

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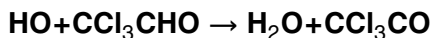
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.25 \times 10^{-11} \exp[-(600 \pm 90)/T]$	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		
<i>Relative Rate Coefficients</i>			
$(1.63 \pm 0.29) \times 10^{-12}$	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)

## 5 Comments

- (a) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO}$  in  $\text{CH}_3\text{ONO}-\text{CCl}_3\text{CHO}$ -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

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from the photolysis of  $\text{CCl}_3\text{CHO}$ . The concentrations of  $\text{CCl}_3\text{CHO}$  and ethyl acetate were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CCl}_3\text{CHO})/k(\text{HO}+\text{ethyl acetate})$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+\text{ethyl acetate})=1.6\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (Atkinson, 1989).

(b) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO}$  or  $\text{C}_2\text{H}_5\text{ONO}$  in  $\text{CH}_3\text{ONO}$  (or  $\text{C}_2\text{H}_5\text{ONO}$ )- $\text{CCl}_3\text{CHO}$ -toluene-air mixtures at  $987\pm 13$  mbar pressure. The concentrations of  $\text{CCl}_3\text{CHO}$  and toluene were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CCl}_3\text{CHO})/k(\text{HO}+\text{toluene})$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+\text{toluene})=5.63\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K (Calvert et al., 2002).

(c) HO radicals were generated by the photolysis of  $\text{O}_3$  in the presence of water vapor in  $\text{O}_3\text{-H}_2\text{O-CCl}_3\text{CHO-2-methylpropane}$ -air mixtures at  $\sim 1$  bar pressure. The concentrations of  $\text{CCl}_3\text{CHO}$  and 2-methylpropane were measured by GC. The measured rate coefficient ratio  $k(\text{HO}+\text{CCl}_3\text{CHO})/k(\text{HO}+2\text{-methylpropane})=0.45\pm 0.01$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO}+2\text{-methylpropane})=2.12\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K (Atkinson, 2003).

**Preferred Values** $k=8.0\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K. $k=1.8\times 10^{-12}\text{ exp}(-240/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  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

5 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  $\text{CCl}_3\text{CHO}$ , as well as for erroneously low measured rate coefficients because of wall adsorption losses of  $\text{CCl}_3\text{CHO}$ . The concentrations of  $\text{CCl}_3\text{CHO}$  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).

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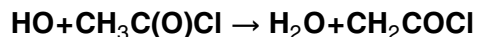
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**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$6.8 \times 10^{-14}$	298±3	Nelson et al., 1984; 1990	RR (a)

**Comments**

(a) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO}$  in  $\text{CH}_3\text{ONO-NO-CH}_3\text{C}(\text{O})\text{Cl-CHCl}_3$  (the reference compound)-air mixtures at 987 mbar pressure. The concentrations of  $\text{CH}_3\text{C}(\text{O})\text{Cl}$  and  $\text{CHCl}_3$  were monitored during the experiments by GC. The measured rate coefficient ratio of  $k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{Cl})/k(\text{HO} + \text{CHCl}_3) \sim 0.65$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{CHCl}_3) = 1.05 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC, current recommendation).

**Preferred Values**

$k = 6.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

**Reliability**

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

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## 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 Fig. 2 of Nelson et al. (1984) and in Fig. 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  $[(9.1 \pm 3.2) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$  at  $298 \pm 3 \text{ K}$ , inconsistent with the data presented in their Fig. 5 and with the data presented in Nelson et al. (1984).

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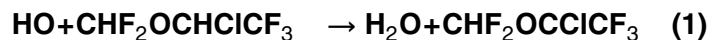
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### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.1 \pm 0.7) \times 10^{-14}$	298	Brown et al., 1989; 1990	DF-RF
$1.12 \times 10^{-12} \exp[-(1280 \pm 50)/T]$	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
$4.5 \times 10^{-13} \exp[-(940 \pm 100)/T]$	293–393	Beach et al., 2001	DF-RF
$(1.9 \pm 0.2) \times 10^{-14}$	293		
<i>Relative Rate Coefficients</i>			
$< 3 \times 10^{-13}$	300 ± 3	McLoughlin et al., 1993	RR (a)

### 5 Comments

(a) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO-NO-CHF}_2\text{OCHClCF}_3$ -diethyl ether air mixtures at ~1 bar pressure. The concentrations of  $\text{CHF}_2\text{OCHClCF}_3$  and diethyl ether were measured by GC. The measured upper limit to the rate coefficient ratio  $k(\text{HO} + \text{CHF}_2\text{OCHClCF}_3)/k(\text{HO} + \text{diethyl ether})$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO} + \text{diethyl ether}) = 1.31 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K (Atkinson, 1994).

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## Preferred Values

$k = 1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.1 \times 10^{-12} \exp(-1280/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–430 K.

## 5 *Reliability*

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

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

## *Comments on Preferred Values*

10 The study of Tokuhashi et al. (1999) used samples of  $\text{CHF}_2\text{OCHClCF}_3$  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  $\text{CHF}_2\text{OCF}_2\text{CHFCI}$  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.

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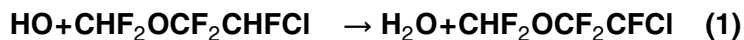
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### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.7 \pm 0.5) \times 10^{-14}$	302	Brown et al., 1989; 1990	DF-RF
$(4.7 \pm 0.7) \times 10^{-14}$	422		
$7.46 \times 10^{-13} \exp[-(1230 \pm 80)/T]$	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
<i>Relative Rate Coefficients</i>			
$< 3 \times 10^{-13}$	300 ± 3	McLoughlin et al., 1993	RR (a)

### 5 Comments

(a) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO-NO-CHF}_2\text{OCF}_2\text{CHFCl}$ -diethyl ether air mixtures at  $\sim 1$  bar pressure. The concentrations of  $\text{CHF}_2\text{OCF}_2\text{CHFCl}$  and diethyl ether were measured by GC. The measured upper limit to the rate coefficient ratio  $k(\text{HO} + \text{CHF}_2\text{OCF}_2\text{CHFCl})/k(\text{HO} + \text{diethyl ether})$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO} + \text{diethyl ether}) = 1.31 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K (Atkinson, 1994).

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## Preferred Values

$k = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 7.5 \times 10^{-13} \exp(-1230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–430 K.

### 5 **Reliability**

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

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

### **Comments on Preferred Values**

10 The study of Tokuhashi et al. (1999) used samples of  $\text{CHF}_2\text{OCF}_2\text{CHFCl}$  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  $\text{CHF}_2\text{OCF}_2\text{CHFCl}$  sample used  
15 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.

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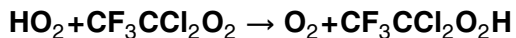
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**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(1.9 \pm 0.7) \times 10^{-12}$	298	Hayman et al., 1994	LP-UVA (a)

5 **Comments**

(a) Laser flash photolysis-UV absorption study of  $\text{CF}_3\text{CCl}_3\text{-CH}_3\text{OH-O}_2\text{-N}_2$  mixtures. The kinetic data were obtained by analyzing two sets of transient decays for  $\text{CF}_3\text{CCl}_2\text{O}_2$  and  $\text{HO}_2$  radicals on the basis of a mechanism consisting of 10 reactions.

10 **Preferred Values**

$k = 1.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

**Reliability**

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

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## 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<sub>2</sub> radicals, that while the  $\alpha$ -substitution of Cl appears to reduce the rate coefficient slightly, the presence of the CF<sub>3</sub> group causes a much larger reduction in the value of  $k$ .

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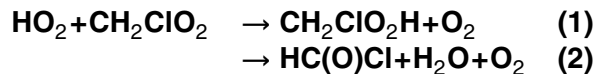
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Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.26 \times 10^{-13} \exp[(822 \pm 63)/T]$ $(4.9 \pm 0.6) \times 10^{-12}$	251–600 298	Catoire et al., 1994	FP-UVA (a)
<i>Branching Ratios</i>			
$k_1/k = 0.27 \pm 0.05$ $k_2/k = 0.73 \pm 0.12$	295	Wallington et al., 1996	UVP-FTIR (b)

5 **Comments**

(a) Flash photolysis-UV absorption study of  $\text{Cl}_2\text{-CH}_3\text{Cl-CH}_3\text{OH-O}_2\text{-N}_2$  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  $\text{CH}_2\text{ClO}_2$  and  $\text{HO}_2$  radicals.

10 (b) Steady-state photolysis of  $\text{Cl}_2\text{-CH}_3\text{Cl-H}_2\text{-O}_2\text{-N}_2$  mixtures at total pressures of 933 mbar with FTIR spectroscopic monitoring of the removal of  $\text{CH}_3\text{Cl}$  and formation of  $\text{CH}_2\text{ClO}_2\text{H}$  and  $\text{HCOCl}$  as a function of the initial concentration ratio  $[\text{H}_2]/[\text{CH}_3\text{Cl}]$ .

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## Preferred Values

$k=5.0\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

$k=3.2\times 10^{-13}\exp(820/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 250–600 K.

$k_1/k=0.3$

5  $k_2/k=0.7$

## Reliability

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

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

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

10  $\Delta(k_2/k)=\pm 0.15$  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  $\text{CH}_3\text{Cl}$  (Sanhueza and Heicklen, 1975; Niki et al., 1980), in which near-quantitative formation of  $\text{HCOCl}$  was observed, even though  $\text{CH}_2\text{ClO}_2$  was believed to be partially removed by reaction with  $\text{HO}_2$ . Tentative observation of  $\text{CH}_2\text{ClO}_2\text{H}$  at yields up to ca. 10% in these earlier studies is also consistent with the branching ratios reported by Wallington et al. (1996).

20 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  $\text{CH}_2\text{ClO}_2$  and  $\text{CH}_3\text{O}_2$  radicals with the  $\text{HO}_2$  radical at 298 K are similar, as are their temperature dependences. This is in marked contrast to the self reactions of  $\text{CH}_2\text{ClO}_2$  and  $\text{CH}_3\text{O}_2$

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radicals where chlorine substitution greatly enhances the rate coefficient. Confirmation of the above data is required.

## References

5 Catoire, V., Lesclaux, R., Lightfoot, P. D., and Rayez, M.-T.: J. Phys. Chem. 98, 2889, 1994.

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10 Wallington, T. J., Hurley, M. D., and Schneider, W. F.: Chem. Phys. Lett. 251, 164, 1996.

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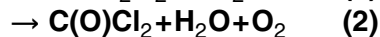
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## IV.A2.149

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.6 \times 10^{-13} \exp[(700 \pm 64)/T]$	286–440	Catoire et al., 1996	FP-UVA (a)
$(5.46 \pm 0.77) \times 10^{-12}$	300		
<i>Branching Ratios</i>			
$k_2/k = 0.71$	295	Catoire et al., 1996	UVP-FTIR (b)
$k_3/k = 0.29$			

5 **Comments**

(a) Flash photolysis of  $\text{CHCl}_3$  in the presence of  $\text{CH}_3\text{OH-O}_2\text{-N}_2$  mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from  $\text{CHCl}_2\text{O}_2$  and  $\text{HO}_2$ ) 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  $\text{CHCl}_2\text{O}_2$ , using a five reaction mechanism.

(b) Steady-state photolysis of  $\text{Cl}_2$  or  $\text{F}_2$  in the presence of  $\text{CH}_2\text{Cl}_2\text{-H}_2\text{-O}_2\text{-N}_2$  mixtures at a total pressure of 933 mbar with FTIR spectroscopic monitoring of the removal of  $\text{CH}_2\text{Cl}_2$  and formation of  $\text{HCOCl}$  and  $\text{COCl}_2$  as a function of the initial concentration ratio  $[\text{H}_2]/[\text{CH}_2\text{Cl}_2]$ .

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## Preferred Values

$k=5.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k=5.6 \times 10^{-13} \exp(700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 280–440 K.

$k_2/k=0.7$  at 298 K.

5  $k_3/k=0.3$  at 298 K.

## Reliability

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

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

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

10  $\Delta (k_2/k) = \pm 0.1$  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  $\text{C}(\text{O})\text{Cl}_2$  and  $\text{HC}(\text{O})\text{Cl}$  formation, respectively. No evidence for formation of the hydroperoxide,  $\text{CHCl}_2\text{OOH}$ , by channel (1) was obtained. The existence of an alternative channel forming  $\text{O}_2$ ,  $\text{OH}$  and  $\text{CHCl}_2\text{O}$  (and therefore  $\text{HC}(\text{O})\text{Cl}$  from  $\text{CHCl}_2\text{O}$  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.

20 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  $\text{CH}_3\text{O}_2$ ,  $\text{CH}_2\text{ClO}_2$ ,  $\text{CHCl}_2\text{O}_2$  and  $\text{CCl}_3\text{O}_2$  radicals with the  $\text{HO}_2$  radical at 298 K are similar, as are their temperature dependences. This is in marked contrast to the self-reactions, for

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which chlorine substitution greatly enhances the rate coefficient. Confirmation of the above sole determination is required.

## References

- 5 Catoire, V., Lesclaux, R., Schneider, W. F., and Wallington, T. J.: J. Phys. Chem. 100, 14356, 1996.

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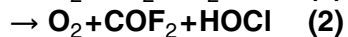
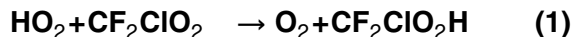
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## IV.A2.150



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.4 \pm 1.7) \times 10^{-12}$	296	Hayman and Battin-Leclerc, 1995	LP-UVA (a)

### 5 Comments

(a) Flash photolysis of  $\text{H}_2\text{O}_2$  in the presence of  $\text{CHF}_2\text{Cl-O}_2\text{-N}_2$  mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from  $\text{CF}_2\text{ClO}_2$  and  $\text{HO}_2$ ) 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

$k = 3.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Reliability

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

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## 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.

- 5 The rate coefficients for the reactions of HO<sub>2</sub> with a number of halogenated peroxy radicals suggest that the presence of an  $\alpha$ -F atom has a deactivating influence. Consistent with this,  $k$  is apparently somewhat lower than those for the corresponding reactions of CH<sub>3</sub>O<sub>2</sub>, CH<sub>2</sub>ClO<sub>2</sub>, CHCl<sub>2</sub>O<sub>2</sub> and CCl<sub>3</sub>O<sub>2</sub>, which all lie in the range  $(5-6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

## 10 References

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

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## IV.A2.151



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.8 \times 10^{-13} \exp[(706 \pm 31)/T]$ $(4.9 \pm 0.6) \times 10^{-12}$	298–374 300	Catoire et al., 1996	FP-UVA (a)
<i>Branching Ratios</i>			
$k_2/k = 1.0$	295	Catoire et al., 1996	UVP-FTIR (b)

### 5 Comments

(a) Flash photolysis of  $\text{CCl}_4$  in the presence of  $\text{CH}_3\text{OH}-\text{O}_2-\text{N}_2$  mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from  $\text{CCl}_3\text{O}_2$  and  $\text{HO}_2$ ) were recorded in the wavelength range 220 nm to 250 nm.  $k$  derived from simulations of the decay traces using a six reaction mechanism.

10 (b) Steady-state photolysis of  $\text{Cl}_2$  or  $\text{F}_2$  in the presence of  $\text{CHCl}_3-\text{H}_2-\text{O}_2-\text{N}_2$  mixtures at a total pressure of 933 mbar with FTIR spectroscopic monitoring of the removal of  $\text{CHCl}_3$  and formation of  $\text{C(O)Cl}_2$  as a function of the initial concentration ratio  $[\text{H}_2]/[\text{CH}_2\text{Cl}_2]$ .  $\text{C(O)Cl}_2$  was the only carbon-containing product observed, with a yield of 100% (within experimental error) under all conditions.

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## Preferred Values

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

$k=4.7 \times 10^{-13} \exp(710/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 280–440 K.

$k_2/k=1.0$  at 298 K.

## 5 *Reliability*

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

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

$\Delta (k_2/k) = {}_{-0.1}^{+0.0}$  at 298 K.

## Comments on Preferred Values

10 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  $\text{CH}_3\text{O}_2$ ,  $\text{CH}_2\text{ClO}_2$ ,  $\text{CHCl}_2\text{O}_2$  and  $\text{CCl}_3\text{O}_2$  radicals with the  $\text{HO}_2$  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  
15 sole determination is required.

## References

20 Catoire, V., Lesclaux, R., Schneider, W. F., and Wallington, T. J.: J. Phys. Chem. 100, 14356, 1996.

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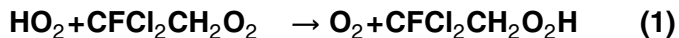
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## IV.A2.152



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.2 \pm 4.6) \times 10^{-12}$	296	Hayman and Battin-Leclerc, 1995	LP-UVA (a)

### 5 Comments

(a) Flash photolysis of  $\text{H}_2\text{O}_2$  in the presence of  $\text{CFCl}_2\text{CH}_3\text{-O}_2\text{-N}_2$  mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from  $\text{CFCl}_2\text{CH}_2\text{O}_2$  and  $\text{HO}_2$ ) 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

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

### Reliability

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

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## 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  $\text{HO}_2$  with  $\text{C}_2\text{H}_5\text{O}_2$ , suggesting that the presence of the  $\text{CFCl}_2$  group has only a minor influence on the reaction.

## References

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

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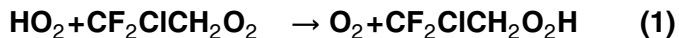
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## IV.A2.153



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.8 \pm 3.4) \times 10^{-12}$	296	Hayman and Battin-Leclerc, 1995	LP-UVA (a)

### 5 Comments

(a) Flash photolysis of  $\text{H}_2\text{O}_2$  in the presence of  $\text{CF}_2\text{ClCH}_3\text{-O}_2\text{-N}_2$  mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from  $\text{CF}_2\text{ClCH}_2\text{O}_2$  and  $\text{HO}_2$ ) 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

$k = 6.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Reliability

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

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## 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<sub>2</sub> with C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>, suggesting that the presence of the CF<sub>2</sub>Cl group has only a minor influence on the reaction.

## References

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

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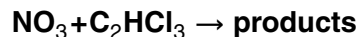
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.0 \times 10^{-13} \exp(-2030/T)$ $(4.43 \pm 0.32) \times 10^{-16}$	278–368 295	Noremsaune et al., 1997	DF-Vis (a)
<i>Relative Rate Coefficients</i>			
$(2.9 \pm 0.2) \times 10^{-16}$	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)

5 **Comments**

(a)  $\text{NO}_3$  was generated by  $\text{F} + \text{HNO}_3$  and detected by optical absorption in a multi-pass cell. Experiments conducted under pseudo-first order conditions.

(b) The relative decay rates of  $\text{C}_2\text{HCl}_3$  and  $\text{C}_2\text{H}_4$  were monitored in  $\text{N}_2\text{O}_5$ - $\text{NO}_2$ -organic-air mixtures at one atmosphere total pressure of air to obtain:  
 $k(\text{NO}_3 + \text{C}_2\text{HCl}_3)/k(\text{NO}_3 + \text{C}_2\text{H}_4) = (1.37 \pm 0.08)$ . This rate coefficient ratio was placed on an absolute basis using  $k(\text{NO}_3 + \text{C}_2\text{H}_4) = 2.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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(c)  $\text{NO}_3$  was formed in the thermal decomposition of  $\text{N}_2\text{O}_5$  in mixtures containing  $\text{C}_2\text{HCl}_3$  and ethene as reference reactant at total pressures of 1013 mbar  $\text{N}_2$ . The addition of ethane as a Cl atom scavenger had no effect.  $k(\text{NO}_3+\text{C}_2\text{HCl}_3)/k(\text{NO}_3+\text{C}_2\text{H}_4)$  was measured to be  $(1.79\pm 0.18)$ . This was placed on an absolute basis using  $k(\text{NO}_3+\text{C}_2\text{H}_4)=2.1\times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation).

(d)  $\text{NO}_3$  was formed in the thermal decomposition of  $\text{N}_2\text{O}_5$  in mixtures containing  $\text{C}_2\text{HCl}_3$  and  $\text{C}_2\text{H}_3\text{Cl}$  as reference reactant at total pressures of 1013 mbar  $\text{N}_2$ . Addition of ethane as a Cl atom scavenger had no effect.  $k(\text{NO}_3+\text{C}_2\text{HCl}_3)/k(\text{NO}_3+\text{C}_2\text{H}_3\text{Cl})$  was measured to be  $(1.3\pm 0.04)$ . This was placed on an absolute basis using  $k(\text{NO}_3+\text{C}_2\text{H}_3\text{Cl})=(3.7\pm 0.8)\times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (Noremsaune et al., 1997).

(e)  $\text{NO}_3$  was formed in the thermal decomposition of  $\text{N}_2\text{O}_5$  in mixtures containing  $\text{C}_2\text{HCl}_3$  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.  $k(\text{NO}_3+\text{C}_2\text{HCl}_3)/k(\text{NO}_3+2,3\text{-dimethylbutane})$  was measured to be  $(0.82\pm 0.21)$ . This was placed on an absolute basis using  $k(\text{NO}_3+2,3\text{-dimethylbutane})=4.39\times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ .

### Preferred Values

$k=3.5\times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

$k=3.2\times 10^{-13}\text{ exp}(-2030/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 270–370 K.

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## Reliability

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

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

## Comments on Preferred Values

5 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-dimethylbutane. 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  
10 at 298 K. There are several product channels open, resulting in formation of trichloroepoxyethane, dichloroacetylchloride, chloroformyl and carbonylchloride (Noremsaune et al., 1995; Perez-Casany et al., 2000).

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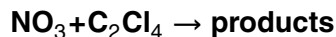
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.6 \pm 8.1) \times 10^{-17}$	295	Noremsaune et al., 1997	DF-Vis (a)
<i>Relative Rate Coefficients</i>			
$< 5 \times 10^{-17}$	298	Atkinson et al., 1987	RR (b)
$(8 \pm 3) \times 10^{-17}$	299	Noremsaune et al., 1997	RR (c)
$4 \times 10^{-17}$	299	Noremsaune et al., 1997	RR (d)
$< 1.8 \times 10^{-16}$	298	Chew et al., 1998	RR (e)

## 5 Comments

(a)  $\text{NO}_3$  generated by  $\text{F} + \text{HNO}_3$  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  $\text{C}_2\text{Cl}_4$  and  $\text{C}_2\text{H}_4$  in  $\text{N}_2\text{O}_5$ - $\text{NO}_2$ -organic-air mixtures at one atmosphere total pressure of air. The observations yielded  $k(\text{NO}_3 + \text{C}_2\text{Cl}_4)/k(\text{NO}_3 + \text{C}_2\text{H}_4) \leq 0.25$ . This upper limit to the rate coefficient ratio was placed on an absolute basis by use of  $k(\text{NO}_3 + \text{C}_2\text{H}_4) = 2.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

(c)  $\text{NO}_3$  formed in the thermal decomposition of  $\text{N}_2\text{O}_5$  in mixtures containing  $\text{C}_2\text{HCl}_3$  and ethene as reference reactant at total pressures of 1013 mbar  $\text{N}_2$ . Addition

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of ethane as Cl atom scavenger had no effect.  $k(\text{NO}_3+\text{C}_2\text{Cl}_4)/k(\text{NO}_3+\text{C}_2\text{H}_4)$  was measured to be  $(0.39\pm 0.11)$ . This was placed on an absolute basis using  $k(\text{NO}_3+\text{C}_2\text{H}_4)=2.1\times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation).

(d)  $\text{NO}_3$  formed in the thermal decomposition of  $\text{N}_2\text{O}_5$  in mixtures containing  $\text{C}_2\text{Cl}_4$  and  $\text{C}_2\text{H}_3\text{Cl}$  as reference reactant at total pressures of 1013 mbar  $\text{N}_2$ . Addition of ethane as Cl atom scavenger had no effect.  $k(\text{NO}_3+\text{C}_2\text{Cl}_4)/k(\text{NO}_3+\text{C}_2\text{H}_3\text{Cl})$  was measured to be 0.1. This was placed on an absolute basis using  $k(\text{NO}_3+\text{C}_2\text{H}_3\text{Cl})=(3.7\pm 0.8)\times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (Noremsaune et al. 1997).

(e)  $\text{NO}_3$  formed in the thermal decomposition of  $\text{N}_2\text{O}_5$  in mixtures containing  $\text{C}_2\text{Cl}_4$  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.  $k(\text{NO}_3+\text{C}_2\text{Cl}_4)/k(\text{NO}_3+2,3\text{-dimethylbutane})$  was measured to be  $(0.21\pm 0.18)$ . This was placed on an absolute basis using  $k(\text{NO}_3+2,3\text{-dimethylbutane})=4.39\times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ .

### Preferred Values

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

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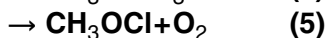
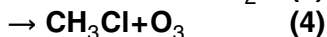
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$$\Delta H^\circ(1) = 4.1 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = 1.2 \text{ kJ mol}^{-1}$$

$$5 \quad \Delta H^\circ(3) = -311.5 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(4) = -49.9 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(5) = -174.6 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.1 \pm 1.7) \times 10^{-12}$	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)
$2.22 \times 10^{-12}$	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		

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Branching Ratios</i>			
$k_1/k > 0.70$	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  $\text{Cl}_2\text{-Cl}_2\text{O-CH}_4\text{-O}_2$  mixtures at  $312 \pm 7$  mbar.  $\text{CH}_3\text{O}_2$  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.  $\text{CH}_3\text{O}_2$  formed in  $\text{F+CH}_4$  in the presence of  $\text{O}_2$ , ClO formed from  $\text{Cl+Cl}_2\text{O}$ , or  $\text{Cl+OCIO}$  or  $\text{Cl+O}_3$ . Both reactants were monitored at their parent ions by mass spectrometry, and the pseudo first order decay of  $\text{CH}_3\text{O}_2$  in excess concentration of ClO used to derive  $k$  directly.

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(c) Flow tube at 2.5 mbar He.  $\text{CH}_3\text{O}_2$  formed in  $\text{F}+\text{CH}_4$  in presence of  $\text{O}_2$ , ClO formed from  $\text{Cl}+\text{O}_3$ . Both reactants were monitored at their parent ions by mass spectrometry, and the pseudo first order decay of  $\text{CH}_3\text{O}_2$  in excess concentration of ClO used to derive  $k$  directly.

(d) Flow tube at 5–6 mbar He.  $\text{CH}_3\text{O}_2$  formed in  $\text{F}+\text{CH}_4$  in presence of  $\text{O}_2$ , ClO formed from  $\text{Cl}+\text{O}_3$ . Both reactants were monitored at their parent ions by mass spectrometry, and the pseudo first order decay of  $\text{CH}_3\text{O}_2$  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 OCIO formation enabled the upper limit of  $k_2/k < 0.05$  to be derived. Also, no evidence for  $\text{O}_3$  formation from channel (4). Observed products by FTIR were HCHO,  $\text{CH}_3\text{OH}$ , HCl and  $\text{HC}(\text{O})\text{OH}$ .  $\text{HC}(\text{O})\text{OH}$  profiles were analysed with the assumption that it was formed in reactions of HCHO with  $\text{HO}_2$  which allows some differentiation between channels (1) and (3), both of which generate HCHO if  $\text{O}_2$  is present, but only one of which generates  $\text{HO}_2$ . The yield of  $\text{HC}(\text{O})\text{OH}$  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 OCIO,  $\text{O}_3$  or  $\text{CH}_3\text{Cl}$ , suggesting that channels 2 and 4 are unimportant. Use of  $\text{CD}_3\text{O}_2$  enabled sensitive measurement of DCl formation, and an upper limit of 2% for channel 3. HCHO, HOCl and  $\text{CH}_3\text{OCl}$  were positively identified as products. Branching ratios were derived by assuming that  $\text{CH}_3\text{OCl}$  is formed directly in channel (5), whereas HCHO and HOCl arise from channel (1) followed by rapid reaction of  $\text{CH}_3\text{O}$  with ClO, and by calibrating the  $\text{CH}_3\text{O}_2$  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  $\text{CH}_3\text{OCl}$  yield was observed.

(g) (see also comment d).  $\text{CH}_3\text{O}_2$  formed in  $\text{F}+\text{CH}_4$  in presence of  $\text{O}_2$ , ClO formed

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from Cl+O<sub>3</sub>. No evidence found for formation of OCIO or CH<sub>3</sub>Cl. Observed products were CH<sub>3</sub>OCl, HOCl and HCHO. Branching ratios for CH<sub>3</sub>OCl and HCHO derived by quantitative mass spectrometric detection of both CH<sub>3</sub>O<sub>2</sub> loss and CH<sub>3</sub>OCl 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<sub>3</sub>O<sub>2</sub> formed in F+CH<sub>4</sub> in presence of O<sub>2</sub>, ClO formed from Cl+Cl<sub>2</sub>O. Branching ratios derived by quantitative mass spectrometric detection of both CH<sub>3</sub>O<sub>2</sub> loss and CH<sub>3</sub>OCl formation.
- (i) Flow tube at 2.7 mbar He. CH<sub>3</sub>O<sub>2</sub> (not detected) formed in F+CH<sub>4</sub> in presence of O<sub>2</sub>, ClO (detected by MS) formed from Cl+O<sub>3</sub>. CH<sub>3</sub>O detected by LIF at 292.8 nm. Derivation of the branching ratio for channel (1) involved modelling CH<sub>3</sub>O profiles that were influenced by the presence of CH<sub>3</sub>O impurity in the CH<sub>3</sub>O<sub>2</sub> source, and reactions of both CH<sub>3</sub>O<sub>2</sub> and CH<sub>3</sub>O with Cl atoms, and loss of CH<sub>3</sub>O by reaction with ClO and at the wall.
- (j) Flow tube at 1.3 mbar He. CH<sub>3</sub>O<sub>2</sub> formed in F+CH<sub>4</sub> in presence of O<sub>2</sub>, ClO (detected by MS) formed from Cl + O<sub>3</sub>. CH<sub>3</sub>O was detected quantitatively by LIF at 298.3 nm, and CH<sub>3</sub>OCl was observed but not quantified. As in comment (i), derivation of the branching ratio required numerical simulation of several processes.

### Preferred Values

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

$$k=2.4 \times 10^{-12} \exp(-20/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220\text{--}360 \text{ K.}$$

$k_1/k=0.73$  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.

## 5 **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.

10  $\Delta (k_5/k) = 0.1$  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  $\text{CH}_3\text{O}_2$  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  $k(200 \text{ K}) < 4.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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  $k(298 \text{ K})$ .

Although there is consensus that formation of  $\text{CH}_3\text{Cl}$ ,  $\text{O}_3$ ,  $\text{OCIO}$  and  $\text{HCl}$  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  $\text{CH}_3\text{OCl}$  formation (5), as  $\text{CH}_3\text{OCl}$  is easiest

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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  $\text{CH}_3\text{O}$  formation in channel (1), which required extensive modelling of its further reactions, and which had to take its presence as impurity in the  $\text{CH}_3\text{O}_2$  source into account (see comments i and j). There are also indirect measurements, which assume rapid conversion of  $\text{CH}_3\text{O}$  to  $\text{HCHO}$  and  $\text{HOCl}$  via reaction with the excess  $\text{ClO}$ , 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  $\text{HCHO}$  and  $\text{HOCl}$ , with kinetics consistent with formation in channel (1) as rate limiting step. Although only  $\text{HCHO}$  could be accurately calibrated,  $\text{HOCl}$  signals were consistent with expected ionization efficiencies compared to  $\text{ClO}$ . The data of Kukui et al. (1994) suffered from a large background under the  $\text{HCHO}$  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  $\text{HOCl}$  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  $\text{CH}_3\text{O}$  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  $\text{CH}_3\text{OOCl}$  association complex on both a singlet surface (decomposing to  $\text{CH}_3\text{O}+\text{ClOO}$ , (1)) or a triplet surface (rearranging to form  $\text{CH}_3\text{OCl} + \text{O}_2$  (2)), which is consistent with experimental

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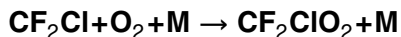
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$$\Delta H^\circ = -127.4 \text{ kJ mol}^{-1}$$

### 5 Low-pressure rate coefficients

#### Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.4 \times 10^{-29} (T/298)^{-5.2} [\text{N}_2]$	200–300	Forst and Caralp, 1991	(a)

#### Comments

- 10 (a) Microcanonical variational theory with inversion of partition functions, used for interpolation between experimental data of the reactions  $\text{O}_2 + (\text{CCl}_3, \text{CCl}_2\text{F} \text{ and } \text{CF}_3)$ .

#### Preferred Values

$k_0 = 1.4 \times 10^{-29} (T/300)^{-5} [\text{N}_2] \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200–300 K.

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## Reliability

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

$\Delta n = \pm 3$ .

## Comments on Preferred Values

- 5 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  $\text{CF}_3 + \text{O}_2$  and  $\text{CFCl}_2 + \text{O}_2$  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

### 10 Rate coefficient data

$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$7.1 \times 10^{-12} (T/298)^{-0.56}$	200–300	Forst and Caralp, 1991	(a)

## Comments

(a) See comment (a) for  $k_0$ .

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## Preferred Values

$k_{\infty} = 7 \times 10^{-12} (T/298)^{-0.6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200–300 K.

## Reliability

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

5  $\Delta n = \pm 0.5$ .

## Comments on Preferred Values

See Comments on Preferred Values for  $k_0$ .

## References

10 Forst, W. and Caralp, F.: J. Chem. Soc. Faraday Trans., 87, 2307, 1991.

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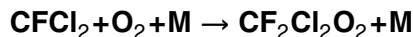
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$$\Delta H^\circ = -124.6 \text{ kJ mol}^{-1}$$

5 **Low-pressure rate coefficients****Rate coefficient data**

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.0 \pm 0.8) \times 10^{-30} [\text{N}_2]$	298	Caralp and Lesclaux, 1983	PP-MS (a)
$5.5 \times 10^{-30} (T/298)^{-6} [\text{N}_2]$	233–373	Danis, 1991	PLP-MS (b)

**Comments**

(a) Pulsed laser photolysis-MS study. Falloff curve measured over the range 0.3–16 mbar, extrapolated with  $F_c = 0.6$  and  $k_\infty = 6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

(b) As comment (a). Results cited and evaluated by Forst and Caralp (1991).

**Preferred Values**

$k_0 = 6 \times 10^{-30} (T/298)^{-6} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230–380 K.

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## Reliability

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

$\Delta n = \pm 3$ .

## Comments on Preferred Values

- 5 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  $\text{CCl}_3 + \text{O}_2$  and  $\text{CF}_3 + \text{O}_2$  would only slightly modify the extrapolated values of  $k_0$  but be of larger influence on  $k_\infty$ .

## High-pressure rate coefficients

### 10 Rate coefficient data

$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6 \pm 1) \times 10^{-12}$	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  $k_0$

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## Preferred Values

$k_{\infty}=9\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 230–300 K.

## Reliability

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

5  $\Delta n=\pm 1$ .

## 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  $k_{\infty}$  by a factor of 1.5. The present choice, therefore, is based on the data from Caralp and Lesclaux (1983) and  $F_c \approx 0.4$ .

## 10 References

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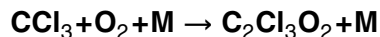
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$$\Delta H^\circ = -92 \text{ kJ mol}^{-1}$$

5 **Low-pressure rate coefficients****Rate coefficient data**

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.8 \pm 0.6) \times 10^{-31} [\text{He}]$	295	Ryan and Plumb, 1984	DF-MS (a)
$(1.6 \pm 0.3) \times 10^{-30} (T/298)^{-6.3} [\text{N}_2]$	233-333	Danis et al., 1991	PLP-MS/UVA (b)
$(6.5 \pm 0.2) \times 10^{-31} (T/300)^{-6.1} [\text{N}_2]$	298-333	Fenter et al., 1993	PLP-MS/UVA (c)
$(2.7 \pm 0.2) \times 10^{-31} (T/300)^{-8.7} [\text{He}]$	286-332	Nottingham et al., 1994	F-MS (d)
$(1.1 \pm 0.3) \times 10^{-30} (T/300)^{-6.3} [\text{N}_2]$	260-346	Luther et al., 2001	PLP-UVA (e)
$(4.2 \pm 0.7) \times 10^{-31} (T/298)^{-6.9} [\text{He}]$			

**Comments**

(a) Microwave discharge flow-quadrupole MS study.  $\text{CCl}_3$  radicals generated by the reaction  $\text{F} + \text{CHCl}_3 \rightarrow \text{CCl}_3 + \text{HF}$ . Falloff curve studied between 2.3 and 7 mbar of He and extrapolated with  $F_c = 0.25$ .

(b) Laser photolysis of  $\text{CCl}_4$  with MS detection at lower and UV absorption detection at higher pressures. Measurements between 1 and 16 mbar as well as at

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930 mbar of  $N_2$ . Evaluation with  $F_c = \exp(-T/255)$ , i.e.,  $F_c = 0.31$  at 300 K, and  $k_\infty = 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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  $k_\infty = 2.6 \times 10^{-12} \exp(T/300)^{-1.1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

(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  $k_\infty = 2.74 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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  $k_\infty = 5.2 \times 10^{-12} (T/300)^{-1.4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

### Preferred Values

$k_0 = 1.1 \times 10^{-30} (T/300)^{-6.2} [N_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.1 \times 10^{-12}$	300	Cooper et al., 1980	PR-UVA (a)
$2.5 \times 10^{-12}$	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  $\text{CCl}_4$  at 930 mbar of He.  $\text{CCl}_3\text{O}_2$  radicals detected by UV absorption.

(b) See comment (a) for  $k_0$ .

(c) See comment (b) for  $k_0$ .

(d) See comment (c) for  $k_0$ .

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(e) See comment (e) for  $k_0$ .

## Preferred Values

$k_\infty = 5.2 \times 10^{-12} (T/300)^{-1.4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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  $k_\infty$  are preferred. The small temperature dependence of  $F_c$  employed by Luther et al. (2001) may be neglected.

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R=alkyl, halogenated alkyl, H or halogen atom.

### Rate coefficient data

Reaction Number	Reactions	$k_1/k_2$ , cm <sup>3</sup> molecule <sup>-1</sup>	Temp./K	Reference	Comments
IV.A2.160	CHFCIO+O <sub>2</sub> → COFCI+HO <sub>2</sub>	(1) $k_1[\text{O}_2] \ll k_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1993	(a)
IV.A2.161	CHFCIO+M → HCOF+Cl+M	(2)			
IV.A2.162	CF <sub>2</sub> CIO+O <sub>2</sub> → products	(1) $k_1[\text{O}_2] \ll k_2$ (933 mbar,air)	298	Edney and Driscoll, 1992	(b)
IV.A2.163	CF <sub>2</sub> CIO+M → COF <sub>2</sub> +Cl+M	(2) $k_2=7.0 \times 10^5$ $k_2=3 \times 10^{13} \exp(-5250/T) (k/s^{-1})$	298	Carr et al., 1986; Rayez et al., 1987	FP-UVA
IV.A2.164	CFCI <sub>2</sub> O+O <sub>2</sub> → products	(1) $k_1[\text{O}_2] \ll k_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1993	(c)
IV.A2.165	CFCI <sub>2</sub> O+M → COFCI+Cl+M	(2) $k_2=7.0 \times 10^5$ $k_2=3 \times 10^{13} \exp(-5250/T) (k/s^{-1})$		Lesclaux et al., 1987; Rayez et al., 1987	FP-MS
IV.A2.166	CCl <sub>3</sub> O+M → COCl <sub>2</sub> +Cl+M	(2) $k_2=8.0 \times 10^6$ $k_2=4 \times 10^{13} \exp(-4600/T) (k/s^{-1})$		Lesclaux et al., 1987; Rayez et al., 1987	FP-MS(c)
IV.A2.167	CF <sub>2</sub> CICH <sub>2</sub> O+O <sub>2</sub> → CF <sub>2</sub> CICHCHO+HO <sub>2</sub>	(1) $k_1[\text{O}_2] \gg K_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1994	(d)
IV.A2.168	CF <sub>2</sub> CICH <sub>2</sub> O+M → CF <sub>2</sub> Cl+HCHO+M	(2)			
IV.A2.169	CFCI <sub>2</sub> CH <sub>2</sub> O+O <sub>2</sub> → CFCI <sub>2</sub> CHO+HO <sub>2</sub>	(1) $k_1[\text{O}_2] \gg K_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1994	(e)
IV.A2.170	CFCI <sub>2</sub> CH <sub>2</sub> O+M → CFCI <sub>2</sub> +HCHO+M	(2) $k_1=2.0 \times 10^{-15}$ $k_1=1.3 \times 10^{-16}$ $k_1=2.4 \times 10^{-15} \exp[-(944 \pm 55)/T]$	298 298 251-341	Mörs et al., 1996; Wu and Carr, 1996	(f) (g)
IV.A2.171	CF <sub>3</sub> CFCIO+O <sub>2</sub> → products	(1) $k_1[\text{O}_2] \ll K_2$ (933 mbar,air)	298	Edney and Driscoll, 1992	(h)
IV.A2.172	CF <sub>3</sub> CFCIO+M → CF <sub>3</sub> COF+Cl+M	(2) $k_1[\text{O}_2] \ll k_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1993	(i)

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Reaction Number	Reactions	$k_1/k_2 \text{ cm}^3 \text{ molecule}^{-1}$	Temp./K	Reference	Comments
IV.A2.173	$\text{CF}_3\text{CCl}_2\text{O} + \text{O}_2 \rightarrow \text{products}$	(1) $k_1[\text{O}_2] \ll k_2$ (933 mbar,air)	298	Edney et al., 1991	(j)
IV.A2.174	$\text{CF}_3\text{CCl}_2\text{O} + \text{M} \rightarrow \text{CF}_3\text{COCl} + \text{Cl} + \text{M}$	(2) $k_1[\text{O}_2] \ll k_2$ (135 mbar, $\text{O}_2$ ) $k_1[\text{O}_2] \ll k_2$ (986 mbar,air) $k_1[\text{O}_2] \ll K_2$ ( $\sim 1$ bar,air)	298 298 298	Sato and Nakamura, 1991 Tuazon and Atkinson, 1993 Hayman et al., 1994	(k) (l) (m)
IV.A2.175	$\text{CF}_3\text{CF}_2\text{CCl}_2\text{O} + \text{O}_2 \rightarrow \text{products}$	(1) $k_1[\text{O}_2] \ll k_2$ (135 mbar, $\text{O}_2$ )	298	Sato and Nakamura, 1991	(n)
IV.A2.176	$\text{CF}_3\text{CF}_2\text{CCl}_2\text{O} + \text{M} \rightarrow \text{CF}_3\text{CF}_2\text{COCl} + \text{Cl} + \text{M}$	(2) $k_1[\text{O}_2] \ll K_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1994	(o)
IV.A2.177	$\text{CF}_2\text{CICF}_2\text{CFCIO} + \text{O}_2 \rightarrow \text{products}$	(1) $k_1[\text{O}_2] \ll k_2$ (135 mbar, $\text{O}_2$ )	298	Sato and Nakamura, 1991	(p)
IV.A2.178	$\text{CF}_2\text{CICF}_2\text{CFCIO} + \text{M} \rightarrow \text{CF}_2\text{CICF}_2\text{COF} + \text{Cl} + \text{M}$	(2) $k_1[\text{O}_2] \ll k_2$ (986 mbar,air)	298	Tuazon and Atkinson, 1994	(q)
IV.A2.179	$\text{CH}_2\text{ClO} + \text{O}_2 \rightarrow \text{HCOCi} + \text{HO}_2$	(1) $4.6 \times 10^{-18}$ (933 mbar, $\text{O}_2 + \text{N}_2$ )	296	Kaiser and Wallington, 1994	(r)
IV.A2.180	$\text{CH}_2\text{ClO} + \text{M} \rightarrow \text{HCO} + \text{HCl} + \text{M}$	(2) $k_1 = 1.3 \times 10^{-12} \exp[-(934 \pm 128)/T]$ $k_2 = 7.7 \times 10^9 \exp[-(4803 \pm 722)/T]$ (13 mbar)	265–306 265–306	Wu and Carr, 2001	(s)
IV.A2.181	$\text{CH}_3\text{CHClO} + \text{O}_2 \rightarrow \text{CH}_3\text{COCl} + \text{HO}_2$	(1) $k_1[\text{O}_2] \ll k_2$ (933 mbar,air)	295	Shi et al., 1993	(t)
IV.A2.182	$\text{CH}_3\text{CHClO} + \text{M} \rightarrow \text{CH}_3\text{CO} + \text{HCl} + \text{M}$	(2) $k_1[\text{O}_2] \ll k_2$ (1013 mbar,air)	298	Maricq et al., 1993	(u)
IV.A2.183	$\text{HOCH}_2\text{CHClO} + \text{O}_2 \rightarrow \text{HOCH}_2\text{COCl} + \text{HCl} + \text{HO}_2$	(1) $k_1[\text{O}_2] \ll k_2$ (986 mbar,air)	298	Tuazon et al., 1988	(v)
IV.A2.184	$\text{HOCH}_2\text{CHClO} + \text{M} \rightarrow \text{CH}_2\text{OH} + \text{HCOCi} + \text{M}$	(2)			
IV.A2.185	$\text{HOCHClCH}_2\text{O} + \text{O}_2 \rightarrow \text{HOCHClCHO} + \text{HO}_2$	(1) $k_1[\text{O}_2] \ll k_2$ (986 mbar,air)	298	Tuazon et al., 1988	(v)
IV.A2.186	$\text{HOCHClCH}_2\text{O} + \text{M} \rightarrow \text{CHClOH} + \text{HCHO} + \text{M}$	(2)			

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IV.A2.187	$\text{CH}_3\text{CCl}_2\text{O} + \text{O}_2 \rightarrow \text{products}$	(1) $k_1[\text{O}_2] \ll k_2$ (933 mbar, $\text{O}_2$ )	298	Nelson et al., 1990	(w)
IV.A2.188	$\text{CH}_3\text{CCl}_2\text{O} + \text{M} \rightarrow \text{CH}_3\text{COCl} + \text{Cl} + \text{M}$	(2)			
IV.A2.189	$\text{CCl}_3\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CCl}_3\text{CHO} + \text{HO}_2$	(1) $k_1[\text{O}_2] \ll k_2$ (933 mbar, $\text{O}_2$ )	298	Nelson et al., 1990	(x)
IV.A2.190	$\text{CCl}_3\text{CH}_2\text{O} + \text{M} \rightarrow \text{CCl}_3 + \text{HCHO} + \text{M}$	(2)			
IV.A2.191	$\text{CCl}_3\text{CCl}_2\text{O} + \text{O}_2 \rightarrow \text{products}$	(1) $k_1[\text{O}_2] \ll k_2$	298	Sato and Nakamura, 1991	(y)
IV.A2.192	$\text{CCl}_3\text{CCl}_2\text{O} + \text{M} \rightarrow \text{CCl}_3\text{COCl} + \text{Cl} + \text{M}$	(2)			

## Comments

- (a) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_2\text{FCI}$ -air mixtures (986 mbar) with FTIR absorption spectroscopic analyses: a 100% yield of  $\text{HCOF}$  was observed, consistent with  $k_1[\text{O}_2] \ll k_2$ .
- (b) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CHF}_2\text{Cl}$ -air mixtures (933 mbar) with FTIR absorption spectroscopic analysis: a  $111 \pm 6\%$  yield of  $\text{COF}_2$  was observed, consistent with  $k_1[\text{O}_2] \ll k_2$ . 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  $\text{CHFCI}_2$  a 100% yield of  $\text{COF}_2$  was observed, consistent with  $k_1[\text{O}_2] \ll k_2$ . 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  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{CF}_2\text{Cl}$ -air mixtures (986 mbar) with FTIR absorption spectroscopic analyses: an  $\sim 100\%$  yield of  $\text{CF}_2\text{ClCHO}$  was observed, consistent with  $k_1[\text{O}_2] \ll k_2$ .

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- (e) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{CFCl}_2$ -air mixtures (986 mbar) with FTIR absorption spectroscopic analysis: an  $\sim 100\%$  yield of  $\text{CFCl}_2\text{CHO}$  was observed, consistent with  $k_1[\text{O}_2] \gg k_2$ . 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;  $\text{CFCl}_2\text{CH}_2\text{O}$  produced by  $\text{CFCl}_2\text{CH}_2\text{O}_2 + \text{NO}$  reaction.
- (g) UV flash photolysis of  $\text{CFCl}_2\text{CH}_3/\text{N}_2/\text{O}_2$  mixtures (13–50 mbar); growth and decay of  $\text{CFCl}_2\text{CH}_2\text{O}$  radicals in excess  $\text{O}_2$  measured by time resolved MS.
- (h) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CF}_3\text{CHFCl}$ -air mixtures (1 atm) with FTIR absorption spectroscopic analyses: a  $100 \pm 4\%$  yield of  $\text{CF}_3\text{C}(\text{O})\text{F}$  was observed, consistent with  $k_1[\text{O}_2] \ll k_2$ .
- (i) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CF}_3\text{CHFCl}$ -air mixtures at 986 mbar total pressure with FTIR absorption spectroscopic analyses: a  $101 \pm 1\%$  yield of  $\text{CF}_3\text{C}(\text{O})\text{F}$  was observed, consistent with  $k_1[\text{O}_2] \gg k_2$ .
- (j) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CF}_3\text{CHCl}_2$ -air mixtures (933 mbar) with FTIR absorption spectroscopic analyses: a  $\sim 100\%$  yield of  $\text{CF}_3\text{C}(\text{O})\text{Cl}$  was observed, consistent with  $k_1\text{O}_2 \ll k_2$ .
- (k) Similar experiments to those of Comment (j) at a total pressure of 133 mbar. The observed formation of  $\text{CF}_3\text{C}(\text{O})\text{Cl}$  is consistent with  $k_1[\text{O}_2] \ll k_2$ .
- (l) Similar experiments to those of Comment (i) at a total pressure of 986 mbar, but with  $\text{CF}_3\text{CHCl}_2$ : a 98% yield of  $\text{CF}_3\text{C}(\text{O})\text{Cl}$  was observed, consistent with  $k_1[\text{O}_2] \ll k_2$ .
- (m) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CF}_3\text{CHCl}_2$ -air mixtures ( $\sim 1$  atm) with broad-band UV absorption analyses: a  $\sim 100\%$  yield of  $\text{CF}_3\text{C}(\text{O})\text{Cl}$  was observed, consistent with  $k_1[\text{O}_2] \ll k_2$ .

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- (n) Similar experiments to those of Comment (k) at a total pressure of 133 mbar. The observed formation of  $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{Cl}$  is consistent with  $k_1[\text{O}_2] \ll k_2$ .
- (o) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CF}_3\text{CF}_2\text{CHCl}_2$ -air mixtures at 986 mbar with FTIR spectroscopic analyses: a 100% yield of  $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{Cl}$  was observed, consistent with  $k_1[\text{O}_2] \ll k_2$ .
- (p) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CHFClCF}_2\text{CF}_2\text{Cl}$ - $\text{O}_2$  mixtures (133 mbar) with FTIR spectroscopic analyses: observed formation of  $\text{CF}_2\text{ClCF}_2\text{C}(\text{O})\text{F}$  is consistent with  $k_1[\text{O}_2] \ll k_2$ .
- (q) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CF}_2\text{ClCF}_2\text{CHFCl}$ -air mixtures (986 mbar) with FTIR spectroscopic analysis: a 99% yield of  $\text{CF}_2\text{ClCF}_2\text{C}(\text{O})\text{F}$  was observed, consistent with  $k_1[\text{O}_2] \ll k_2$ .
- (r) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Cl}$ - $\text{O}_2$ - $\text{N}_2$  mixtures with FTIR absorption spectroscopic analysis of  $\text{HOCl}$ ,  $\text{CO}$ ,  $\text{HCl}$  and  $\text{CH}_2\text{ClCOOH}$  products.  $k_1/k_2$  based on yields of  $\text{CO}$  and  $\text{HOCl}$ , 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  $\text{HCOCl}$  and  $\text{HCl}$  products used to determine kinetics.
- (t) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{C}_2\text{H}_5\text{Cl}$ - $\text{O}_2$ - $\text{N}_2$  mixture with FTIR spectroscopic analysis of products: the observed high yields of  $\text{HCl}$  (157%) and  $\text{CO}_2$  (53%) were explained by reaction (2).
- (u) Laser flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{C}_2\text{H}_5\text{Cl}$ -air mixtures with infrared absorption detection of  $\text{HCl}$ . The observed secondary formation of  $\text{HCl}$  was explained by reaction (2).

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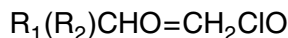
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(v) Steady-state photolysis of  $\text{CH}_3\text{ONO}$  or  $\text{C}_2\text{H}_5\text{ONO}$  in the presence of chloroethene -NO-air mixtures, with and without  $\text{C}_2\text{H}_6$  as an added Cl atom scavenger. FTIR spectroscopic analysis of 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  $k_1[\text{O}_2]$  and  $k_2$  shown above.

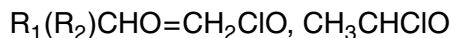
(w) Steady-state photolysis of  $\text{CH}_3\text{CCl}_3\text{-O}_2$  mixtures in the presence of  $\text{Br}_2$  or NO (to scavenge Cl atoms), with GC and IR analyses of products.  $\text{CH}_3\text{COCl}$  was the major product observed, consistent with the relative values of  $k_1[\text{O}_2]$  and  $k_2$  shown above.

(x) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{CCl}_3\text{-O}_2$  mixtures with GC and IR analyses of  $\text{CCl}_3\text{CHO}$  and  $\text{COCl}_2$ , which are consistent with the relative values of  $k_1[\text{O}_2]$  and  $k_2$  shown above.

(y) Steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CHCl}_2\text{CCl}_3\text{-O}_2$  mixtures (133 mbar) with FTIR spectroscopic analysis. The observed formation yields of  $\text{CCl}_3\text{COCl}$  and  $\text{COCl}_2$  are consistent with  $k_1[\text{O}_2] \ll k_2$ .

**Preferred Values**

$$k_1/k_2=4.6\times 10^{-18}\text{ cm}^3\text{ molecule}^{-1}\text{ at }298\text{ K.}$$

**Comments on Preferred Values**

The elimination of HCl occurs from the  $\text{CH}_3\text{CHClO}$  radical (Shi et al., 1993, Maricq et al., 1993) as well as from the  $\text{CH}_2\text{ClO}$  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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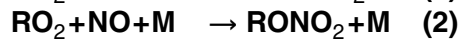
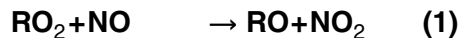
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## IV.A2.193-202



(R= CH<sub>2</sub>Cl, CHFCI, CF<sub>2</sub>Cl, CFCI<sub>2</sub>, CCl<sub>3</sub>, CH<sub>3</sub>CFCI, CF<sub>2</sub>CICH<sub>2</sub>, CFCI<sub>2</sub>CH<sub>2</sub>, CF<sub>3</sub>CCl<sub>2</sub>, CH<sub>2</sub>CICH<sub>2</sub>)

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

Reaction Number	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>				
IV.A2.193	R=CH <sub>2</sub> Cl (1.87±0.20)×10 <sup>-11</sup>	295	Sehested et al., 1993	PR-AS (a)
IV.A2.194	R=CHFCI (1.31±0.20)×10 <sup>-11</sup>	299	Bhatnagar and Carr, 1996	FP-MS (b)
IV.A2.195	R=CF <sub>2</sub> Cl 1.6×10 <sup>-11</sup> (T/298) <sup>-(1.5±0.4)</sup> (1.6±0.3)×10 <sup>-11</sup>	230-430 298	Dognon et al., 1985	PLP-MS (c)
IV.A2.196	R=CFCl <sub>2</sub> (1.31±0.12)×10 <sup>-11</sup> (1.6±0.2)×10 <sup>-11</sup>	295 298	Sehested et al., 1993 Lesclaux and Caralp, 1984	PR-AS (a) PLP-MS (d)
	1.45×10 <sup>-11</sup> (T/298) <sup>-(1.3±0.2)</sup> (1.45±0.2)×10 <sup>-11</sup>	230-430 298	Dognon et al., 1985	PLP-MS (c)
IV.A2.197	R=CCl <sub>3</sub> (1.86±0.28)×10 <sup>-11</sup> 1.7×10 <sup>-11</sup> (T/298) <sup>-(1.0±0.2)</sup> (1.7±0.2)×10 <sup>-11</sup>	295 230-430 298	Ryan and Plumb, 1984 Dognon et al., 1985	DF-MS (e) PLP-MS (c)

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Reaction Number	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
IV.A2.198	R=CH <sub>3</sub> CFCl $2.0 \times 10^{-11} (T/300)^{-(1.8 \pm 0.3)}$ $1.9 \times 10^{-11}$	263-321 298	Wu and Carr, 1996	FP-MS (f)
IV.A2.199	R=CF <sub>2</sub> ClCH <sub>2</sub> $(1.18 \pm 0.10) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
IV.A2.200	R=CFCl <sub>2</sub> CH <sub>2</sub> $(1.28 \pm 0.11) \times 10^{-11}$ $1.3 \times 10^{-11} (T/300)^{-(1.5 \pm 0.2)}$ $1.25 \times 10^{-11}$	295 263-321 298	Sehested et al., 1993 Wu and Carr, 1996	PR-AS (a) FP-MS (f)
IV.A2.201	R=CF <sub>3</sub> CCl <sub>2</sub> $(1.5-2.0) \times 10^{-11}$	298	Hayman et al., 1994	PLP-AS (g)
IV.A2.202	R=CH <sub>2</sub> ClCH <sub>2</sub> $(9.7 \pm 1.2) \times 10^{-12}$	298	Patchen et al., 2005	F-CIMS (h)

## Comments

- (a)  $k$  determined from  $+d[\text{NO}_2]/dt$  at a total pressure of 1 bar.
- (b) Photolysis of Cl<sub>2</sub> in the presence of CH<sub>2</sub>FCI, O<sub>2</sub>, N<sub>2</sub> and NO at 8–33 mbar total pressure.  $k$  was obtained from the formation kinetics of NO<sub>2</sub>.  $k$  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  $\text{CH}_3\text{CFCl}_2$  in the presence of  $\text{O}_2$ ,  $\text{N}_2$  and  $\text{NO}$  at 11–27 mbar total pressure.  $k$  for both  $\text{CH}_3\text{CFClO}_2$  and  $\text{CFCl}_2\text{CH}_2\text{O}_2$  were extracted simultaneously from the removal kinetics of  $\text{NO}$  and formation kinetics of  $\text{CFCl}_2\text{CH}_2\text{O}$ .  $k$  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)  $\text{CH}_2\text{ClCH}_2\text{O}_2$  generated from the  $\text{C}_2\text{H}_4 + \text{Cl}$  reaction, with  $k$  determined from pseudo-first order decay  $\text{CH}_2\text{ClCH}_2\text{O}_2$  in the presence of  $\text{NO}$ . Measurements made at 130 mbar pressure.

### Preferred Values



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

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



$$k=1.3\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}\text{ at }298\text{ K.}$$

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



$$k=1.5\times 10^{-11}\left(T/298\right)^{-1.5}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}\text{ over the temperature range }230\text{--}430\text{ K.}$$

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

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

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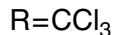


$k=1.5 \times 10^{-11} (T/298)^{-1.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230–430 K.

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

$\Delta n = \pm 0.5$ .

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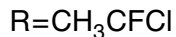


$k=1.8 \times 10^{-11} (T/298)^{-1.0} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230–430 K.

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

$\Delta n = \pm 0.5$ .

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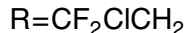


$k=2.0 \times 10^{-11} (T/298)^{-1.8} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 260–320 K.

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

$\Delta n = \pm 0.5$ .

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

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

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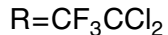


$k=1.3 \times 10^{-11} (T/298)^{-1.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 260–320 K.

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

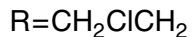
$\Delta n = \pm 0.5$ .

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$k=1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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



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

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

### **Comments on Preferred Values**

5 R=CF<sub>2</sub>CICH<sub>2</sub>, CH<sub>2</sub>Cl

The preferred values are the rounded-off rate coefficients determined by Sehested et al. (1993).

R=CHFCI

10 The preferred value is the rounded-off rate coefficient determined by Bhatnagar and Carr (1996).

R=CF<sub>2</sub>Cl

15 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=CFCI<sub>2</sub>

20 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<sub>3</sub>CFCI

25 The preferred values are based on the temperature dependent data of Wu and Carr (1996).

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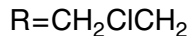
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The preferred value is the rounded-off average of the rate coefficients determined by Sehested et al. (1993) and Wu and Carr (1996).



The preferred value is the mid-point of the range of values determined by Hayman et al. (1994).



10 The preferred value is the rate coefficient determined by Patchen et al. (2005).

$R = \text{CCl}_3$  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).

15 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,  $\text{CH}_3\text{O}_2$  and  $\text{C}_2\text{H}_5\text{O}_2$ , indicates that the presence of a  $\alpha$ -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  $\alpha$ -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  $\text{NO}_2$  greater than unity for all the  $\text{RO}_2$  radicals studied; suggesting that the  $\text{RO}_2 + \text{NO}$  reactions mainly form RO and  $\text{NO}_2$ , with additional  $\text{NO}_2$  being produced from secondary chemistry. Recently, Nishida et al. (2004) have observed formation of a small yield  $1.7 \pm 0.3\%$  of  $\text{CF}_3\text{ONO}_2$  from the reaction of  $\text{CF}_3\text{O}_2$  with NO, confirming the existence of channel (2) at 930 mbar pressure. This

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suggests that the reactions of the C<sub>1</sub> and C<sub>2</sub> halogenated RO<sub>2</sub> radicals will generally have minor channels forming RONO<sub>2</sub>, but additional studies are required to confirm this.

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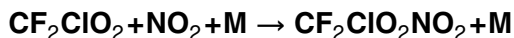
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$$\Delta H^\circ = -107 \text{ kJ mol}^{-1}$$

### 5 Low-pressure rate coefficients

#### Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.8 \pm 1.8) \times 10^{-29} [\text{O}_2]$	298	Moore and Carr, 1990	FP-MS (a)
$(5.0 \pm 1.0) \times 10^{-29} (T/298)^{-6.2} [\text{O}_2]$	248-324	Wu and Carr, 1991	FP-MS (b)

#### Comments

10 (a)  $\text{CF}_2\text{ClO}_2$  radicals generated by flash photolysis of  $\text{CF}_2\text{ClBr}$  in the presence of  $\text{O}_2$  and detected by MS. Measurements over the pressure range 1.3–13 mbar, extrapolated with  $F_c=0.6$  and  $k_\infty=5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

(b) As comment (a).  $F_c=0.78 \exp(-T/569)$ , i. e.,  $F_c(298)=0.46$ , and  $k_\infty=4.5 \times 10^{-12} (T/298)^{-2.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  used for extrapolation.

#### Preferred Values

15  $k_0=5 \times 10^{-29} (T/298)^{-6.2} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ cm}^3$  over the temperature range 250–320 K.

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## Reliability

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

$\Delta n = \pm 2$ .

## Comments on Preferred Values

- 5 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,
- 10 assuming equal values of  $k_0$  for the bath gases  $O_2$  and  $N_2$ .

## High-pressure rate coefficients

### Rate coefficient data

$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.2 \times 10^{-12}$	298	Moore and Carr, 1990	(a)
$4.5 \times 10^{-12} (T/298)^{-2.5}$	248–324	Wu and Carr, 1991	(b)

## Comments

- 15 (a) See comment (a) for  $k_0$ .

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(b) See comment (b) for  $k_0$ . The measurements were performed so far from the high pressure range that extrapolations were uncertain.

### Preferred Values

$k_\infty = 6.3 \times 10^{-12} (T/298)^{-0.7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–320 K.

### 5 *Reliability*

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

$\Delta n = \pm 0.5$ .

### Comments on Preferred Values

10 The unusually large negative temperature coefficient of  $k_\infty$  derived by Wu and Carr (1991) signals problems with the falloff extrapolations. For this reason it appears safer to employ the falloff curves for  $\text{CF}_2\text{ClO}_2\text{NO}_2$  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  $\text{CF}_3\text{O}_2 + \text{NO}_2$ . As for the reverse reaction,  $F_c = 0.30$  is recommended.

15

### 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.

20 Köppenkastrop, D. and Zabel F.: Int. J. Chem. Kinet., 23, 1, 1991.

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Moore, S. M. and Carr, R. W.: J. Phys. Chem., 94, 1393, 1990.

Wu, F. and Carr, R. W.: Int. J. Chem. Kinet., 23, 701, 1991.

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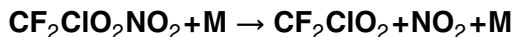
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$$\Delta H^\circ = 107 \text{ kJ mol}^{-1}$$

5 **Low-pressure rate coefficients****Rate coefficient data**

$k_0/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.8 \times 10^{-3} \exp(-10500/T) [\text{N}_2]$	273–288	Köppenkastrup and Zabel, 1991	(a)
$1.1 \times 10^{-3} \exp(-10762/T) [\text{N}_2]$	276–289	Xiong and Carr, 1994	(b)

**Comments**

10 (a) Thermal decomposition of  $\text{CF}_2\text{ClO}_2\text{NO}_2$  in a temperature-controlled ( $\pm 0.1^\circ\text{C}$ ) 420 liter reaction chamber. The reactant was monitored in situ by long-path IR absorption.  $\text{N}_2$  pressures of 11, 82, and 800 mbar were employed. Falloff extrapolations with  $F_c = 0.30$  and  $k_\infty = 1.6 \times 10^{16} \exp(-11990/T) \text{ s}^{-1}$ .

15 (b) Continuous-flow temperature-controlled ( $\pm 1^\circ\text{C}$ ) photoreactor coupled to MS.  $\text{N}_2$  pressures of 4–53 mbar were employed. Falloff extrapolations made with  $F_c = 0.45$  and  $k_\infty = 6.7 \times 10^{16} \exp(-11871/T) \text{ s}^{-1}$ .

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## Preferred Values

$k_0 = 1.8 \times 10^{-3} \exp(-10\,500/T) [\text{N}_2] \text{ s}^{-1}$  over the temperature range 270–290 K.

## Reliability

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

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

## Comments on Preferred Values

10 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  $k_\infty$ . 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  $k_\infty$  such as given below.

## 15 High-pressure rate coefficients

### Rate coefficient data

$k_\infty/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.6 \times 10^{16} \exp(-11\,990/T)$	273–288	Köppenkastrop and Zabel, 1991	(a)
$6.7 \times 10^{16} \exp(-11\,871/T)$	276–289	Xiong and Carr, 1994	(b)

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## Comments

(a) See comment (a) for  $k_0$ .

(b) See comment (b) for  $k_0$ . The given value for  $k_\infty$  actually stems from a combination of recombination data, equilibrium constants and theoretical modelling. It is consistent with the observed pressure dependence.

## Preferred Values

$k_\infty = 1.6 \times 10^{16} \exp(-11\,990/T) \text{ s}^{-1}$  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.

Destriau, M. and Troe, J.: Int. J. Chem. Kinet., 22, 915, 1990.

Köppenkastrop, D. and Zabel F.: Int. J. Chem. Kinet., 23, 1, 1991.

Xiong, J. Q. and Carr, R. W.: J. Phys. Chem., 98, 9811, 1994.

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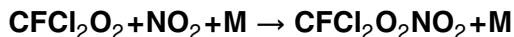
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$$\Delta H^\circ = -107 \text{ kJ mol}^{-1}$$

5 **Low-pressure rate coefficients****Rate coefficient data**

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.5 \pm 0.5) \times 10^{-29} [\text{O}_2]$	298	Lesclaux and Caralp, 1984	PLP-MS (a)
$(3.5 \pm 0.5) \times 10^{-29} (T/298)^{-4.1} [\text{O}_2]$	233–373	Lesclaux et al., 1986	PLP-MS (b)
$(5.5 \pm 1.6) \times 10^{-29} (T/298)^{-5.5} [\text{O}_2]$	233–373	Caralp et al., 1988	PLP-MS (c)

**Comments**

(a) Pulsed laser photolysis with MS detection of  $\text{CFCl}_2\text{O}_2$ . Pressure range 1.3–13 mbar. Falloff extrapolation with  $F_c=0.6$  and  $k_\infty=6.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

(b) As comment (a). Falloff extrapolation with  $F_c=0.6$  and  $k_\infty=5.9 \times 10^{-12} (T/298)^{-0.72} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

(c) As comment (a). Falloff extrapolation using  $F_c=\exp(-T/342)$ , i.e.  $F_c=0.42$  at 298 K, and  $k_\infty=8.3 \times 10^{-12} (T/298)^{-0.66} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

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## Preferred Values

$k_0 = 5.5 \times 10^{-29} (T/298)^{-5.5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230–380 K.

## Reliability

- 5  $\Delta \log k_0 = \pm 0.3$  at 298 K.  
 $\Delta n = \pm 2$ .

## Comments on Preferred Values

10 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  $\text{O}_2$  and  $\text{N}_2$  are assumed.

## High-pressure rate coefficients

### Rate coefficient data

$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.0 \pm 1.0) \times 10^{-12}$	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  $k_0$ .

## 5 Preferred Values

$k_\infty = 8.3 \times 10^{-12} (T/298)^{-0.66} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230–380 K.

## Reliability

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

10  $\Delta n = \pm 0.5$ .

## Comments on Preferred Values

See Comments on Preferred Values for  $k_0$ .

## References

- 15 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.

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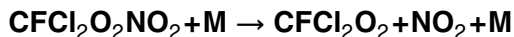
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$$\Delta H^\circ = 107 \text{ kJ mol}^{-1}$$

## 5 Low-pressure rate coefficients

### Rate coefficient data

$k_0/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.0 \times 10^{-2} \exp(-10860/T) [\text{N}_2]$	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  $k_\infty = 6.6 \times 10^{16} \exp(-12240/T) \text{ s}^{-1}$ .

### Preferred Values

$k_0 = 1.0 \times 10^{-2} \exp(-10860/T) [\text{N}_2] \text{ s}^{-1}$  over the temperature range 260–300 K.

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## Reliability

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

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

## Comments on Preferred Values

- 5 The 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

$k_\infty/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.0 \times 10^{16} \exp(-12300/T)$	274–305	Simonaitis et al., 1979	(a)
$6.0 \times 10^{16} \exp(-12240/T)$	260–300	Köppenkastrop and Zabel, 1991	(b)

## 10 Comments

(a) Steady-state photolysis of  $\text{Cl}_2\text{-CHFCl}_2\text{-O}_2\text{-NO-NO}_2$  mixtures at 1 bar. Simulation of the mechanism depending on the extent of various Cl-consuming reactions.  $k$  was assumed to be close to  $k_\infty$ .

(b) See comment (a) for  $k_0$ .

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## Preferred Values

$k_{\infty}=6.6\times 10^{16} \exp(-12\,240/T) \text{ s}^{-1}$  over the temperature range 260–300 K.

## Reliability

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

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

## 10 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.

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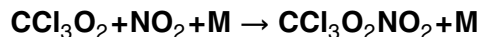
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$$\Delta H^\circ = -105.6 \text{ kJ mol}^{-1}$$

5 **Low-pressure rate coefficients****Rate coefficient data**

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.2 \pm 3) \times 10^{-29} (T/298)^{-6.0} [\text{O}_2]$	233-373	Caralp et al., 1988	PLP-MS (a)

**Comments**

- 10 (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  $k_\infty = 1.49 \times 10^{-12} (T/298)^{-0.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

**Preferred Values**

$k_0 = 9.2 \times 10^{-29} (T/298)^{-6.0} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230–380 K.

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## Reliability

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

$\Delta n = \pm 2$ .

## Comments on Preferred Values

- 5 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

### 10 Rate coefficient data

$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.49 \pm 0.8) \times 10^{-12} (T/298)^{-0.3}$	233–373	Caralp et al., 1988	PLP-MS (a)

## Comments

(a) See comment (a) for  $k_0$ .

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## Preferred Values

$k_{\infty}=1.5\times 10^{-12} (T/298)^{-0.7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230–380 K.

## Reliability

- 5  $\Delta \log k_{\infty}=\pm 0.3$  at 298 K.  
 $\Delta n=\pm 0.5$

## Comments on Preferred Values

- 10 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.  
15 Destriau, M. and Troe, J.: Int. J. Chem. Kinet., 22, 915, 1990.

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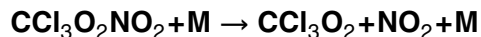
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$$\Delta H^\circ = 105.6 \text{ kJ mol}^{-1}$$

### 5 Low-pressure rate coefficients

#### Rate coefficient data

$k_0/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$6.3 \times 10^{-3} \exp(-10235/T) [\text{N}_2]$	260-300	Köppenkastrop and Zabel, 1991	(a)

#### Comments

(a) Thermal decomposition of  $\text{CCl}_3\text{O}_2\text{NO}_2$  studied in a temperature-controlled 410 l reaction chamber. The reactant was monitored by in situ long-path IR absorption. Pressures of  $\text{N}_2$  of 11, 82, and 800 mbar were employed. The data were extrapolated with  $F_c = 0.22$  and  $k_\infty = 4.8 \times 10^{16} \exp(-11820/T) \text{ s}^{-1}$ .

#### Preferred Values

$k_0 = 4.3 \times 10^{-3} \exp(-10235/T) [\text{N}_2] \text{ s}^{-1}$  over the temperature range 260–300 K.

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## Reliability

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

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

## Comments on Preferred Values

- 5 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.

## 10 High-pressure rate coefficients

### Rate coefficient data

$k_\infty/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.42 \times 10^{16} \exp(-11\,500/T)$	274-305	Simonaitis et al., 1979	(a)
0.24	298		
$6.6 \times 10^{16} \exp(-12\,240/T)$	260-300	Köppenkastrop and Zabel, 1991	(b)
0.29	298		

## Comments

- 15 (a) Steady-state photolysis of  $\text{Cl}_2\text{-CHCl}_3\text{-O}_2\text{-N}_2\text{-NO-NO}_2$  mixtures at 1 bar. Product formation monitored by IR spectroscopy. Some assumption about the mechanism

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had to be made. The reaction was assumed to be at the high pressure limit.

(b) See comment (a) for  $k_0$ .

### Preferred Values

$k_\infty = 4.8 \times 10^{16} \exp(-11\,820/T) \text{ s}^{-1}$  over the temperature range 260–300 K.

### 5 *Reliability*

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

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

### Comments on Preferred Values

10 The two available measurements are in close agreement such that  $k_\infty$  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.

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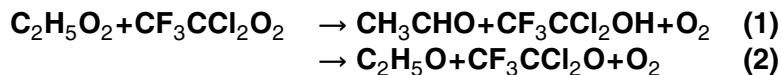
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#### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = (3.6 \pm 0.5) \times 10^{-12}$	298	Hayman et al., 1994	PLP-UVA (a)
$k_2 = (9_{-5}^{+9}) \times 10^{-13}$	298		

#### 5 Comments

(a) Laser flash photolysis-UV absorption study of  $\text{CF}_3\text{CCl}_3\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$  mixtures. Kinetic data were obtained by analyzing two sets of transient decays on the basis of a mechanism consisting of 13 reactions.

#### Preferred Values

10  $k_1 = 3.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.  
 $k_2 = 9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

#### Reliability

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

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## 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.

### 5 References

Hayman, G. D., Jenkin, M. E., Murrells, T. P., and Johnson, C. E.: Atmos. Environ., 28A, 421, 1994.

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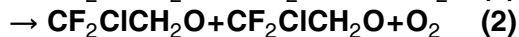
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#### IV.A2.210



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = (4.13 \pm 0.58) \times 10^{-12}$	298	Wallington and Nielsen, 1991	FP-UVA (a,b)
<i>Branching Ratios</i>			
$k_2/k \approx 1.0$	298	Tuazon and Atkinson, 1994	UV-P-FTIR (e)

#### 5 Comments

(a)  $k_{\text{obs}}$  is based on the measured overall second-order decay of  $\text{CF}_2\text{CICH}_2\text{O}_2$ , defined by  $-\text{d}[\text{CF}_2\text{CICH}_2\text{O}_2]/\text{dt} = 2k_{\text{obs}} [\text{CF}_2\text{CICH}_2\text{O}_2]^2$ . As described in detail by Lesclaux (1997),  $\text{HO}_2$  radicals formed from the subsequent chemistry of  $\text{CF}_2\text{CICH}_2\text{O}$  (formed from channel (2)) are expected to lead to secondary removal of  $\text{CF}_2\text{CICH}_2\text{O}_2$ . The true value of  $k$  is expected to fall in the range  $k_{\text{obs}}/(1+\alpha) < k < k_{\text{obs}}$  where  $\alpha = k_2/k$ .

(b) Pulse radiolysis study of  $\text{CF}_2\text{CICH}_3\text{-O}_2\text{-SF}_6$  mixtures over the pressure range 150–1000 mbar.  $\text{CF}_2\text{CICH}_2\text{O}_2$  radicals were monitored by UV absorption with  $\sigma_{250\text{nm}} = (3.38 \pm 0.68) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .

(c) Photolysis of  $\text{Cl}_2$  in the presence of  $\text{CF}_2\text{CICH}_3\text{-air}$  mixtures at 987 mbar pressure. In situ monitoring of reactants and products by FTIR spectroscopy was consistent

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with formation of CF<sub>2</sub>CICHO with a yield ca. 100%, once corrections were made for secondary removal.

### Preferred Values

$k_1 = 2.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

5  $k_2/k = 1.0$  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.

### 10 *Comments on Preferred Values*

The observed formation of CF<sub>2</sub>CICHO in ca. 100% yield from CF<sub>2</sub>CICH<sub>3</sub> 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<sub>2</sub>CICH<sub>2</sub>O with O<sub>2</sub> to form CF<sub>2</sub>CICHO and HO<sub>2</sub>. This also indicates that secondary removal of CF<sub>2</sub>CICH<sub>2</sub>O<sub>2</sub> by reaction with HO<sub>2</sub> must generate CF<sub>2</sub>CICHO as the major carbon-containing product, in a similar fashion to the observed dominant formation of HC(O)Cl from the reaction of HO<sub>2</sub> with CH<sub>2</sub>ClO<sub>2</sub> (Wallington et al., 1996).

15 The preferred value of  $k$  at 298 K is derived from the  $k_{\text{obs}}$  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.  $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k$  is estimated to be  $k_{\text{obs}} / (1 + 0.5(k_2/k))$ , with this approximation assuming that the secondary reaction of HO<sub>2</sub> with CF<sub>2</sub>CICH<sub>2</sub>O<sub>2</sub> competes equally with its removal via

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$\text{HO}_2 + \text{HO}_2$ . The reliability range reflects that  $k$  has been derived by this approximate procedure. Confirmatory kinetics and product studies are required.

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5 Lesclaux, R.: Combination of peroxy radicals in the gas phase, in: Peroxy Radicals, edited by: Alfassi, Z. B., John Wiley and Sons, 1997.

Tuazon, E. C. and Atkinson, R.: Environ. Sci. Technol., 28, 2306, 1994.

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Wallington, T. J., Hurley, M. D., and Schneider, W. F.: Chem. Phys. Lett., 251, 164, 1996.

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#### IV.A2.211



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = (4.36 \pm 0.64) \times 10^{-12}$	298	Wallington and Nielsen, 1991	PR-UVA (a,b)
<i>Branching Ratios</i>			
$k_2/k \approx 1.0$	298	Tuazon and Atkinson, 1994	UV-P-FTIR (e)

#### 5 Comments

(a)  $k_{\text{obs}}$  is based on the measured overall second-order decay of  $\text{CFCl}_2\text{CH}_2\text{O}_2$ , defined by  $-\text{d}[\text{CFCl}_2\text{CH}_2\text{O}_2]/\text{dt} = 2k_{\text{obs}} [\text{CFCl}_2\text{CH}_2\text{O}_2]^2$ . As described in detail by Lesclaux (1997),  $\text{HO}_2$  radicals formed from the subsequent chemistry of  $\text{CFCl}_2\text{CH}_2\text{O}$  (formed from channel (2)) are expected to lead to secondary removal of  $\text{CFCl}_2\text{CH}_2\text{O}_2$ . The true value of  $k$  is expected to fall in the range  $k_{\text{obs}}/(1+\alpha) < k < k_{\text{obs}}$  where  $\alpha = k_2/k$ .

(b) Pulse radiolysis study of  $\text{CFCl}_2\text{CH}_3\text{-O}_2\text{-SF}_6$  mixtures over the pressure range 152–1013 mbar.  $\text{CFCl}_2\text{CH}_2\text{O}_2$  radicals were monitored by UV absorption with  $\sigma_{250 \text{ nm}} = (3.38 \pm 0.68) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .

(c) Photolysis of  $\text{Cl}_2$  in the presence of  $\text{CFCl}_2\text{CH}_3\text{-air}$  mixtures at 987 mbar pressure. In situ monitoring of reactants and products by FTIR spectroscopy was consistent

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with formation of  $\text{CFCl}_2\text{CHO}$  with a yield ca. 100%, once corrections were made for secondary removal.

### Preferred Values

$k_1 = 2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

5  $k_2/k = 1.0$  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

10 The observed formation of  $\text{CFCl}_2\text{CHO}$  in ca. 100% yield from  $\text{CFCl}_2\text{CH}_3$  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  $\text{CFCl}_2\text{CH}_2\text{O}$  with  $\text{O}_2$  to form  $\text{CFCl}_2\text{CHO}$  and  $\text{HO}_2$ . This also indicates that secondary removal of  $\text{CFCl}_2\text{CH}_2\text{O}_2$  by reaction with  $\text{HO}_2$  must generate  $\text{CFCl}_2\text{CHO}$  as the major carbon-containing product, in a similar fashion to the observed dominant formation of  $\text{HCOCl}$  from the reaction of  $\text{HO}_2$  with  $\text{CH}_2\text{ClO}_2$  (Wallington et al., 1996).

15 The preferred value of  $k$  at 298 K is derived from the  $k_{\text{obs}}$  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.  $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k$  is estimated to be  $k_{\text{obs}} / (1 + 0.5(k_2/k))$ , with this approximation assuming that the secondary reaction of  $\text{HO}_2$  with  $\text{CFCl}_2\text{CH}_2\text{O}_2$  competes equally with its removal via

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$\text{HO}_2 + \text{HO}_2$ . The reliability range reflects that  $k$  has been derived by this approximate procedure. Confirmatory kinetics and product studies are required.

## References

5 Lesclaux, R.: Combination of peroxy radicals in the gas phase, in: Peroxy 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.

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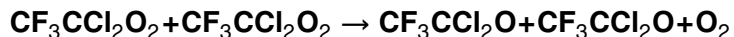
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = (3.33 \pm 0.53) \times 10^{-12}$	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)

## 5 Comments

- (a)  $k_{\text{obs}}$  is based on the measured overall second-order decay of  $\text{CF}_3\text{CCl}_2\text{O}_2$ , defined by  $-\text{d}[\text{CF}_3\text{CCl}_2\text{O}_2]/\text{dt} = 2k_{\text{obs}}[\text{CF}_3\text{CCl}_2\text{O}_2]^2$ .
- (b) Pulse radiolysis study of  $\text{CF}_3\text{CHCl}_2\text{-O}_2\text{-SF}_6$  mixtures over the pressure range of 1013 mbar.  $\text{CF}_3\text{CCl}_2\text{O}_2$  radicals were monitored by UV absorption with  $\sigma_{250\text{nm}} = (1.70 \pm 0.26) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . The derived value of  $k$  was determined from the measured overall second-order decay of  $\text{CF}_3\text{CCl}_2\text{O}_2$  radicals.
- (c)  $\text{CF}_3\text{CCl}_2\text{O}_2$  radicals were generated by 193 nm laser flash photolysis of  $\text{CF}_3\text{CCl}_3\text{-CH}_3\text{OH-O}_2\text{-N}_2$  mixtures and  $\text{CF}_3\text{CCl}_3\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$  mixtures at a total pressure of 1013 mbar.  $\text{CF}_3\text{CCl}_2\text{O}_2$  radicals were monitored by UV absorption in the range 230–270 nm, with  $\sigma_{250\text{nm}} = (1.79 \pm 0.18) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$ .  $k$  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  $\text{CF}_3\text{CCl}_2\text{O}_2$  with  $\text{HO}_2$  and  $\text{C}_2\text{H}_5\text{O}_2$  were determined simultaneously.

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## Preferred Values

$$k=3.5\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}\text{ at }298\text{ K.}$$

## Reliability

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

## 5 *Comments on Preferred Values*

The reported formation of  $\text{CF}_3\text{C}(\text{O})\text{Cl}$  with approximately 100% yield from  $\text{CF}_3\text{CHCl}_2$  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  $\text{CF}_3\text{CCl}_2\text{O}_2$  proceeds essentially exclusively via formation of  $\text{CF}_3\text{CCl}_2\text{O}$  radicals, which decompose by elimination of Cl. This is also supported by the UV spectral study of  $\text{CF}_3\text{CCl}_2\text{O}_2$  by Jemi-Alade et al. (1991), involving flash photolysis-UV absorption of  $\text{Cl}_2$  in the presence of  $\text{CF}_3\text{CHCl}_2$  and  $\text{O}_2$ . In that study, no decay in the absorption due to  $\text{CF}_2\text{CCl}_2\text{O}_2$  was observed over a 40 ms time scale, demonstrating near-quantitative regeneration of Cl atoms, and therefore  $\text{CF}_3\text{CCl}_2\text{O}_2$ , in the system.

15 The kinetics studies of Wallington et al. (1994) and Hayman et al. (1994) reported UV absorption spectra for  $\text{CF}_3\text{CCl}_2\text{O}_2$  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  
20 regeneration of  $\text{CF}_3\text{CCl}_2\text{O}_2$ , and to extract the true value of  $k$ . It is noted that Wallington et al. (1994) made use of concentrations of  $\text{CF}_3\text{CCl}_2\text{O}_2$  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  $\text{CF}_3\text{CCl}_2\text{O}$  and/or Cl might partially preclude regeneration of  $\text{CF}_3\text{CCl}_2\text{O}_2$ , or lead to secondary removal of

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CF<sub>3</sub>CCl<sub>2</sub>O<sub>2</sub>. 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.

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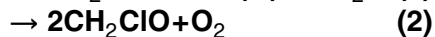
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## IV.A2.213



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = 3.1 \times 10^{-13} \exp[(735 \pm 95)/T]$	228–380	Dagaut et al., 1988	FP-UVA (a,b)
$k_{\text{obs}} = (3.78 \pm 0.45) \times 10^{-12}$	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)
<i>Branching Ratios</i>			
$k_2/k \approx 1.0$	305	Sanhueza and Heicklen, 1975	UVP-IR (e)
$k_2/k \approx 1.0$	298	Niki et al., 1980	UVP-FTIR (f)

### 5 Comments

(a)  $k_{\text{obs}}$  is based on the measured overall second-order decay of  $\text{CH}_2\text{ClO}_2$ , defined by  $-\text{d}[\text{CH}_2\text{ClO}_2]/\text{dt} = 2k_{\text{obs}}[\text{CH}_2\text{ClO}_2]^2$ . As described in detail by Lesclaux (1997),  $\text{HO}_2$  radicals formed from the subsequent chemistry of  $\text{CH}_2\text{ClO}$  (formed from channel (2)) are expected to lead to secondary removal of  $\text{CH}_2\text{ClO}_2$ . The true value of  $k$  is expected to fall in the range  $k_{\text{obs}}/(1+\alpha) < k < k_{\text{obs}}$ , where  $\alpha = k_2/k$ .

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(b) Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Cl-O}_2\text{-N}_2$  mixtures at total pressures of 33–533 mbar at 298 K and of 133 mbar ( $\text{N}_2$ ) from 228–380 K. Peroxy radical concentrations were monitored by UV absorption with  $\sigma_{250\text{ nm}}=(3.14\pm 0.45)\times 10^{-18}\text{ cm}^3\text{ molecule}^{-1}$ .

(c) Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Cl-O}_2\text{-N}_2$  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  $\sigma_{250\text{ nm}}=(3.40\pm 0.20)\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$  in the temperature range 251 to 393 K (decreasing at higher temperatures). Values of  $k_{\text{obs}}/\sigma_{250\text{ nm}}$  are in excellent agreement with those of Dagaout et al. (1988) over the common temperature range. Observed decays in transient absorption were found to be distorted from second order kinetics at wavelengths  $<250\text{ nm}$  where  $\text{HO}_2$  absorbs significantly, allowing  $k$  and the rate coefficient for the reaction of  $\text{HO}_2$  with  $\text{CH}_2\text{ClO}_2$  to be extracted via an iterative procedure.

(d) Experiments performed at pressures in the range 1.3 to 4 mbar.  $\text{CH}_2\text{ClO}_2$  radicals were produced by the  $\text{F}+\text{CH}_3\text{Cl}$  reaction, with subsequent addition of  $\text{O}_2$ .  $\text{CH}_2\text{ClO}_2$  radicals were monitored by titration to  $\text{NO}_2$  following reaction with excess  $\text{NO}$ , with LIF detection of  $\text{NO}_2$ .  $\text{HO}_2$  radicals generated from the subsequent chemistry of  $\text{CH}_2\text{ClO}$  (formed from channel (2)) were also titrated to  $\text{NO}_2$  under the experimental conditions, but were independently measured through detection of simultaneously formed  $\text{HO}$ , by RF.  $k$  values were extracted by numerical simulation of the results, using an 8 reaction scheme.

(e) Photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Cl-O}_2$  mixtures. In situ monitoring of products by IR showed exclusive formation of  $\text{HCl}$  and  $\text{HC(O)Cl}$  as the initial products.

(f) Photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Cl-air}$  mixtures. In situ monitoring of reactants and products by FTIR spectroscopy showed 90–95% conversion of  $\text{CH}_3\text{Cl}$  to  $\text{HC(O)Cl}$ . Tentative observation of  $\text{CH}_2\text{ClOOH}$  at yields up to ca. 10%, and

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H<sub>2</sub>O<sub>2</sub>, is indicative of the occurrence of partial reaction of HO<sub>2</sub> with CH<sub>2</sub>ClO<sub>2</sub> in competition with the HO<sub>2</sub> self reaction.

### Preferred Values

$k = 3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

5  $k = 1.9 \times 10^{-13} \exp(870/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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.

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

10  $\Delta (k_2/k) = \begin{matrix} +0.0 \\ -0.1 \end{matrix}$  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<sub>2</sub>ClO<sub>2</sub> radicals.

15 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  
20 the preferred value of  $k$  at 298 K. As noted above, the earlier  $k_{\text{obs}}$  data of Dagaut et al. (1988) are also in excellent agreement with those of Catoire et al. (1994) when both

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sets of data are analyzed by a simple second-order treatment from results derived at  $\lambda = 250$  nm, and are therefore also consistent with this recommendation.

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1-10) \times 10^{-12}$	300	Catoire et al., 1996	FP-UVA (a)
$(7.0 \pm 1.8) \times 10^{-12}$	298	Biggs et al., 1999	DF-LIF (b)
<i>Branching Ratios</i>			
$k_2/k \geq 0.85$	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)

### 5 Comments

(a) Flash photolysis of  $\text{CHCl}_3$  in the presence of  $\text{CH}_3\text{OH-O}_2\text{-N}_2$  mixtures at a total pressure of 1000 mbar. Decays in transient absorption signals (with contributions from  $\text{CHCl}_2\text{O}_2$  and  $\text{HO}_2$ ) 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  $\text{CHCl}_2\text{O}_2$  with  $\text{HO}_2$ , 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  $\text{CH}_2\text{ClO}_2$  and  $\text{CCl}_3\text{O}_2$  (which are almost identical) in the same laboratory (Catoire et al., 1994; 1996), and recommend that  $k$

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is the average these determinations:  $2.6 \times 10^{-13} \exp[(800 \pm 60)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 273 K to 460 K, with  $k = (3.8 \pm 1.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

- (b) Experiments performed at pressures in the range 1.3 to 4 mbar.  $\text{CHCl}_2\text{O}_2$  radicals were produced by the  $\text{F} + \text{CH}_2\text{Cl}_2$  reaction, with subsequent addition of  $\text{O}_2$ .  $\text{CHCl}_2\text{O}_2$  radicals were monitored indirectly by titration to  $\text{NO}_2$  following reaction with excess  $\text{NO}$ , with LIF detection of  $\text{NO}_2$ .  $\text{ClO}$  radicals generated by the secondary chemistry were also titrated to  $\text{NO}_2$  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  $\text{Cl}_2$  in the presence of  $\text{CH}_2\text{Cl}_2\text{-O}_2\text{-N}_2$  mixtures. In situ monitoring of products by IR showed formation of  $\text{HC(O)Cl}$  as the dominant product as part of an efficient chain mechanism.  $\text{C(O)Cl}_2$  was observed as a minor product. Listed quantum yield based on the reported quantum yield of 5.9 for  $\text{HC(O)Cl}$  formation.
- (d) Photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_2\text{Cl}_2\text{-O}_2\text{-N}_2$  mixtures. In situ monitoring of products by FTIR spectroscopy showed formation of  $\text{HC(O)Cl}$  as the dominant product as part of an efficient chain mechanism.  $\text{C(O)Cl}_2$  was observed as a minor product. Listed quantum yield based on the reported quantum yield of 7.5 for  $\text{HC(O)Cl}$  formation.
- (e) Photolysis of  $\text{Cl}_2$  or  $\text{F}_2$  in the presence of  $\text{CH}_2\text{Cl}_2\text{-O}_2\text{-N}_2$  mixtures. In situ monitoring of products by FTIR spectroscopy showed formation of  $\text{HC(O)Cl}$  and  $\text{C(O)Cl}_2$  with yields of ca. 85% and 5% respectively. No other primary products were detected.
- (f) Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_2\text{Cl}_2\text{-O}_2\text{-N}_2$  mixtures over the temperature range 250 K to 325 K demonstrated efficient chain regeneration of  $\text{CHCl}_2\text{O}_2$  in the system.

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## Preferred Values

$k_2/k=1.0$  at 298 K.

## Reliability

$(k_2/k)=_{-0.15}^{+0.0}$  at 298 K.

### 5 **Comments on Preferred Values**

The reported dominant chain formation of HC(O)Cl from CH<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> proceeds almost exclusively via formation of CHCl<sub>2</sub>O radicals (channel (2)), which decompose by elimination of Cl.

10 This is also supported by the failure to detect CHCl<sub>2</sub>OH in all the product studies, which would otherwise provide evidence for channel (1). The efficient chain regeneration of CHCl<sub>2</sub>O<sub>2</sub> radicals observed in the Cl<sub>2</sub>-CH<sub>2</sub>Cl<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> flash photolysis experiments of Catoire et al. (1996) is also consistent with the dominance of channel (2) over a wide temperature range.

15 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<sub>2</sub>O<sub>2</sub> by reaction with HO<sub>2</sub> was occurring (see note (a) above). The discharge flow determination of Biggs et al. (1999)  
20 was complicated by indirect detection of CHCl<sub>2</sub>O<sub>2</sub> (which also had contributions from ClO), and possible secondary chain removal of CHCl<sub>2</sub>O<sub>2</sub> via reactions with Cl and ClO. Consequently, no firm recommendation for  $k$  is currently possible, and further kinetics studies are required.

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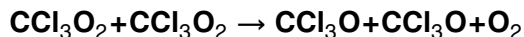
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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.6 \times 10^{-12} (T/298)^{-(3.0 \pm 1.0)}$	253–333	Danis et al., 1991	FP-UVA (a,b)
$3.3 \times 10^{-13} \exp[(745 \pm 58)/T]$	273–460	Catoire et al., 1996	FP-UVA (a,c)
$(4.07 \pm 0.54) \times 10^{-12}$	298		

### 5 Comments

(a)  $k$  is defined by  $-\text{d}[\text{CCl}_3\text{O}_2]/\text{dt} = 2k[\text{CCl}_3\text{O}_2]^2$ .

(b) Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CHCl}_3\text{-O}_2\text{-N}_2$  mixtures at 1013 mbar total pressure.  $k$  was determined from the formation of  $\text{C(O)Cl}_2$ , using UV absorption spectroscopy at 240 nm. Results were consistent with chain formation of  $\text{C(O)Cl}_2$ , resulting from thermal decomposition of  $\text{CCl}_3\text{O}$  to generate  $\text{C(O)Cl}_2$  and regenerate  $\text{Cl}$ .

(c) Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CHCl}_3\text{-O}_2\text{-N}_2$  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  $\text{C(O)Cl}_2$  as part of an efficient chain mechanism. Results were consistent with a chain length of ca. 100. FTIR product studies of the photolysis of  $\text{Cl}_2\text{-CHCl}_3\text{-O}_2\text{-N}_2$  mixtures and  $\text{F}_2\text{-CHCl}_3\text{-O}_2\text{-N}_2$  mixtures also demonstrated 100% formation of  $\text{C(O)Cl}_2$ .

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## Preferred Values

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

$k = 3.3 \times 10^{-13} \exp(740/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270–460 K.

## Reliability

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

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

## Comments on Preferred Values

10 The reported formation of  $\text{C(O)Cl}_2$  with 100% yield from  $\text{CHCl}_3$  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  $\text{CCl}_3\text{O}_2$  proceeds exclusively via formation of  $\text{CCl}_3\text{O}$  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  $\text{Cl}_2$  in the presence of  $\text{CHCl}_3$  and  $\text{O}_2$ . The results demonstrate essentially quantitative regeneration of Cl atoms in the system, the chain length for conversion of  $\text{CHCl}_3$  into  $\text{C(O)Cl}_2$  being ca. 100.

15 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  $\text{C(O)Cl}_2$  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  $\text{CHCl}_3$ . Ethanol is three orders of magnitude more reactive than  $\text{CHCl}_3$  towards Cl, and can therefore scavenge a proportion of Cl atoms when present in trace amounts.

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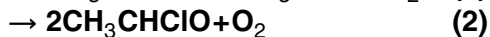
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#### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.2 \pm 1.3) \times 10^{-12}$	295	Maricq et al., 1993	(a,b)
<i>Branching Ratios</i>			
$k_2/k = 0.95 \pm 0.05$	295	Maricq et al., 1993	(b)

#### 5 Comments

(a)  $k$  is defined by  $-\text{d}[\text{CH}_3\text{CHClO}_2]/\text{dt} = 2k[\text{CH}_3\text{CHClO}_2]^2$ .

(b) Pulsed photolysis of  $\text{Cl}_2$  in the presence of  $\text{C}_2\text{H}_5\text{Cl}-\text{O}_2-\text{N}_2$  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

$k_2 = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_2/k = 0.95$  at 298 K.

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## 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

- 5 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.

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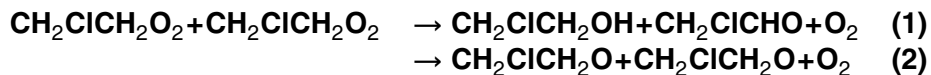
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### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = 1.1 \times 10^{-13} \exp[(1020 \pm 170)/T]$	228–380	Dagaut et al., 1988	FP-UVA (a,b)
$k_{\text{obs}} = (3.57 \pm 0.57) \times 10^{-12}$	298		
$k_{\text{obs}} = (6.0 \pm 0.8) \times 10^{-12}$	295	Maricq et al., 1993	FP-UVA (a,c)
$k_{\text{obs}} = 4.0 \times 10^{-14} \exp[(1376 \pm 60)/T]$	253–345	Chakir et al., 2003	MM-UVA (a,d)
$k_{\text{obs}} = (4.5 \pm 0.4) \times 10^{-14}$			
<i>Branching Ratios</i>			
$k_1/k = 0.31$	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)
$k_2/k = 0.57$			

### 5 Comments

(a)  $k_{\text{obs}}$  is based on the measured overall second-order decay of  $\text{CH}_2\text{ClCH}_2\text{O}_2$ , defined by  $-\text{d}[\text{CH}_2\text{ClCH}_2\text{O}_2]/\text{dt} = 2k_{\text{obs}}[\text{CH}_2\text{ClCH}_2\text{O}_2]^2$ . As described in detail by Lesclaux (1997),  $\text{HO}_2$  radicals formed from the subsequent chemistry of  $\text{CH}_2\text{ClCH}_2\text{O}$  (formed from channel (2)) are expected to lead to secondary removal

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of  $\text{CH}_2\text{ClCH}_2\text{O}_2$ . The true value of  $k$  is expected to fall in the range  $k_{\text{obs}}/(1+\alpha) < k < k_{\text{obs}}$ , where  $\alpha = k_2/k$ .

(b) Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{C}_2\text{H}_4\text{-O}_2\text{-N}_2$  mixtures over the pressure range 33–533 mbar.  $\text{CH}_2\text{ClCH}_2\text{O}_2$  concentrations measured by UV absorption spectroscopy using  $\sigma_{250\text{ nm}} = (3.64 \pm 0.39) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .

(c) Pulsed photolysis of  $\text{Cl}_2$  in the presence of  $\text{C}_2\text{H}_4\text{-O}_2\text{-N}_2$  mixtures at 1013 mbar pressure. Kinetics determined from time-resolved UV absorption spectra of  $\text{CH}_2\text{ClCH}_2\text{O}_2$  and  $\text{HO}_2$ . The values of  $\sigma(\text{CH}_2\text{ClCH}_2\text{O}_2)$  obtained are ca. 13% greater than those reported by Dagaut et al. (1988).

(d) Modulated photolysis of  $\text{Cl}_2$  in the presence of  $\text{C}_2\text{H}_4\text{-O}_2\text{-N}_2$  mixtures over the pressure range 67–267 mbar.  $k_{\text{obs}}$  determined from analysis of modulated absorption waveforms in the wavelength range 215–270 nm. The UV absorption spectrum of  $\text{CH}_2\text{ClCH}_2\text{O}_2$  characterized simultaneously, agrees well with that of Dagaut et al. (1988) at  $\lambda \geq 240 \text{ nm}$ , with  $\sigma_{250\text{ nm}} = (3.56 \pm 0.20) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . At shorter wavelengths, cross sections are up to 20% greater.

(e) Steady-state photolysis of  $\text{Cl}_2\text{-C}_2\text{H}_4\text{-O}_2\text{-N}_2$  mixtures at total pressures of 933 mbar with FTIR spectroscopic monitoring of the removal of  $\text{C}_2\text{H}_4$  and the formation of  $\text{CH}_2\text{ClCHO}$ ,  $\text{CH}_2\text{ClCH}_2\text{OOH}$ , and  $\text{CH}_2\text{ClCH}_2\text{OH}$ . The listed branching ratios were derived from the yields of  $\text{CH}_2\text{ClCH}_2\text{OH}$  and  $\text{CH}_2\text{ClCHO}$  relative to the decay of  $\text{C}_2\text{H}_4$ .

### Preferred Values

$k = 3.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 4.2 \times 10^{-14} \exp(1300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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.

## 5 *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<sub>2</sub> and CH<sub>2</sub>ClCH<sub>2</sub>O<sub>2</sub>, inferred from their modulated photolysis study, to draw conclusions about the temperature dependence of the branching ratio for HO<sub>2</sub> 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  $k_{\text{obs}}$  and  $k_2/k$  using a methodology similar to that employed by Lesclaux (1997) for peroxy radicals with self reaction rate coefficients  $\geq$  ca.  $2 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at room temperature.  $k$  is estimated to be  $k_{\text{obs}}/(1+0.5(k_2/k))$ , with this approximation assuming that the secondary reaction of HO<sub>2</sub> with CH<sub>2</sub>ClCH<sub>2</sub>O<sub>2</sub> competes equally with its removal via HO<sub>2</sub>+HO<sub>2</sub>. 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  $\approx 1$  at the high end of the studied temperature range, 380 K. The 298 K value of  $k_{\text{obs}}$  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<sub>2</sub>ClCH<sub>2</sub>O<sub>2</sub> reported by Maricq et al. (1993).

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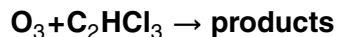
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**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$< 3 \times 10^{-20}$	296	Atkinson et al., 1982	S-CL

**Preferred Values**

$k < 5 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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  $\sim 2$  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  $\text{O}_3$  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.

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- 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 Jr., J. N.: Int. J.

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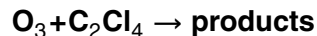
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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<2 \times 10^{-23}$	297	Mathias et al., 1974	(a)

(a) From experiments carried out at initial  $\text{O}_3$  and tetrachloroethene concentrations of  $\geq 10^{17} \text{ molecule cm}^{-3}$  in the presence of excess  $\text{O}_2$ , using an assumed mechanism and monitoring the formation rate of  $\text{C}(\text{O})\text{Cl}_2$ . From the data given in Mathias et al. (1974), a more conservative upper limit of  $k < 8 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  can be derived by assuming that only one  $\text{C}(\text{O})\text{Cl}_2$  molecule is formed per tetrachloroethene reacted.

### Preferred Values

$k < 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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

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(Atkinson and Carter, 1984), which show that Cl atom substitution markedly decreases the reactivity of the chloroethenes towards O<sub>3</sub>, compared to that for ethene.

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Atkinson. R. and Carter, W. P. L.: Chem. Rev., 84, 437, 1984.

5 Mathias, E., Sanhueza, E., Hisatsune, I. C., and Heicklen, J.: Can. J. Chem., 52, 3852, 1974.

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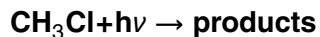
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### Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{Cl} + h\nu \rightarrow \text{CH}_3 + \text{Cl}$	349	343

### 5 Preferred Values

#### Absorption cross-sections for $\text{CH}_3\text{Cl}$ at 295 K and 210 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K <sup>a</sup>	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 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			

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<sup>a</sup>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<sub>3</sub>+Cl. Photochemistry at shorter wavelengths is discussed by Shold and Rebbert (1978) at 216 nm. A H-atom product channel has now been observed using product translational energy studies (Amaral et al., 2001).

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Hubrich, C., Zetzsch, C., and Stuhl, F.: Ber. Bunsenges. Phys. Chem., 81, 437, 1977.  
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Shold, D. M. and Rebbert, R. E.: J. Photochem., 9, 499, 1978.  
Simon, P. C., Gillotay, D., Vanlaethem-Meuree, N., and Wisemberg, J.: J. Atmos. Chem., 7, 107, 1988.

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**CH<sub>3</sub>OCl+hν → products****Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH <sub>3</sub> OCl+hν → CH <sub>3</sub> O+Cl (1)	202.9	589
→ CH <sub>3</sub> +ClO (2)	312.4	383
→ CH <sub>2</sub> OCl+H (3)	417.4	287

5 **Absorption cross-sections for CH<sub>3</sub>OCl 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)

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## 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<sub>2</sub> impurities which were quantified by MS.
- 5 (b) Monochromator/double diode array set up (temperature and resolution not quoted). Impurities (CH<sub>3</sub>OH and Cl<sub>2</sub>) 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 <sup>2</sup>P<sub>1/2</sub> and <sup>2</sup>P<sub>3/2</sub> states. The overall quantum yield of Cl atom generation at 308 nm was measured relative to Cl<sub>2</sub>. The ratio of Cl (<sup>2</sup>P<sub>1/2</sub>) / Cl (<sup>2</sup>P<sub>3/2</sub>) was found to be 0.31±0.02 at 308 nm and 1.45 ±0.05 at 235 nm.
- 10 (d) Crossed laser-molecular beam scattering experiment with detection of photofragments by VUV photoionisation-TOFMS (Cl detected as Cl<sup>+</sup> and CH<sub>3</sub>O as CHO<sup>+</sup>). No other photofragments were observed.

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## Preferred Values

### Absorption cross-sections for CH<sub>3</sub>OCl at 295 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
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

5  $\phi_1 = 1.0$  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

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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

Crowley, J. N., Helleis, F., Müller, R., Moortgat, G. K., and Crutzen, P. J.: J. Geophys. Res., 99, 20683, 1994.

Jungkamp, T. P. W., Kirchner, U., Schmidt, M., and Schindler, R. N.: J. Photochem. Photobiol. A, 91, 1, 1995.

Krisch, M. J., McCunn, L. R., Takematsu, K., Butler, L. J., Blas, F. R., and Shu, J.: J. Phys. Chem. A, 108, 1650, 2004.

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**CHF<sub>2</sub>Cl+hν → products****Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CHF <sub>2</sub> Cl+hν → CHF <sub>2</sub> +Cl (1)	327	327
→ CClF <sub>2</sub> +H (2)	423	283
→ CF <sub>2</sub> +HCl (3)	207	287

5 **Absorption cross-sections for CHF<sub>2</sub>Cl at 298 K and 210 K**

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 298 K <sup>a</sup>	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 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

<sup>a</sup>No temperature dependence at  $\lambda < 188$  nm.**Evaluated kinetic and photochemical data for atmospheric chemistry**

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## Quantum yields for CHF<sub>2</sub>Cl 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<sub>2</sub>Cl 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  $\phi_{\text{H}}/\phi_{\text{total}} = 0.16 \pm 0.05$ . 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.

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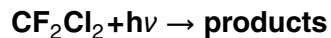
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### Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_2\text{Cl}_2 + h\nu \rightarrow \text{CF}_2\text{Cl} + \text{Cl}$ (1)	346	346
$\rightarrow \text{CF}_2 + 2\text{Cl}$ (2)	542	221

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## Absorption cross-sections for CF<sub>2</sub>Cl<sub>2</sub> at 295 K and 210 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K <sup>a</sup>	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 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

<sup>a</sup>No temperature dependence at  $\lambda \leq 186$  nm.

### 5 Quantum yields for CF<sub>2</sub>Cl<sub>2</sub> photolysis at 298 K

$\phi(1)=1$  over the range 190–225 nm.

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## 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:

$$\sigma_T = \sigma(218) \exp\{4.1 \times 10^{-4} (\lambda - 184.9)(T - 298)\} \quad [\lambda \text{ in nm; } T \text{ in K}].$$

More recently the absorption cross-sections of  $\text{CF}_2\text{Cl}_2$  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  $\text{CF}_2\text{Cl}_2$  at 193 nm, with photoproducts investigated by TOF-MS. Results show exclusive dissociation to  $\text{CF}_2\text{Cl} + \text{Cl}$ , with the  $\text{CF}_2\text{Cl}$  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.

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**CFCI<sub>3</sub>+hν → products****Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ.mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CFCI <sub>3</sub> +hν → CFCI <sub>2</sub> +Cl (1)	317	377
→ CFCI+2Cl (2)	558	214

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## Absorption cross-sections for CFCI<sub>3</sub> at 295 K and 210 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K <sup>a</sup>	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 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			

<sup>a</sup>No temperature dependence at  $\lambda \leq 184$  nm.

## Quantum yields for CFCI<sub>3</sub> photolysis at 298 K

<sup>5</sup>  $\phi(1)=1$  at  $\lambda > 180$  nm.

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## 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:

$$\sigma_T = \sigma(218) \exp\{4.1 \times 10^{-4} (\lambda - 184.9)(T - 298)\} [\lambda \text{ in nm}; T \text{ in K}].$$

Felder and Demuth (1993) studied laser photodissociation of  $\text{CFCl}_3$  at 193 nm using TOF-MS to investigate the nature and energetics of the photofragments. At this wavelength dissociation occurs exclusively to yield  $\text{CFCl}_2 + \text{Cl}$  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.

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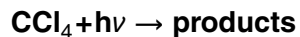
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### Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CCl}_4 + h\nu \rightarrow \text{CCl}_3 + \text{Cl}$ (1)	288	415
$\rightarrow \text{CCl}_2 + 2\text{Cl}$ (2)	577	207

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## Preferred Values

### Absorption cross-sections for CCl<sub>4</sub> at 295 K and 210 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K <sup>a</sup>	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 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			

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<sup>a</sup>No temperature dependence at  $\lambda < 204$  nm.

## Quantum yields for $\text{CCl}_4$ photolysis at 298 K

$\phi(1) = 1$  over wavelength range 174–275 nm.

### 5 *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  $\phi(\text{Cl}) = 1.5 \pm 0.1$  and  $1.9 \pm 0.1$  respectively at these wavelengths (Hanf et al., 2003).

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## Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ.mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{CF}_2\text{Cl} + h\nu \rightarrow \text{CH}_3\text{CF}_2 + \text{Cl}$	335 (est)	360
$\text{CH}_3\text{CF}_2\text{Cl} + h\nu \rightarrow \text{CH}_2\text{CF}_2 + \text{Cl} + \text{H}$	400 (est)	300

## Preferred Values

Absorption cross-sections for  $\text{CH}_3\text{CF}_2\text{Cl}$  at 298 K and 220 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$		$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	
	298 K	220 K		298 K	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

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## 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  $\text{CH}_3\text{CF}_2 + \text{Cl}$  is the main channel, but that C-H bond cleavage also occurs with a branching ratio of about 40%.

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**CH<sub>3</sub>CFCI<sub>2</sub>+hν → products****Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ.mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH <sub>3</sub> CFCI <sub>2</sub> +hν → CH <sub>3</sub> CFCI+Cl	335 (est)	360
→ CH <sub>2</sub> CFCI <sub>2</sub> +H	400 (est)	300

**Preferred Values****Absorption cross-sections for CH<sub>3</sub>CFCI<sub>2</sub> at 298 K and 210 K**

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 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

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## 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 occur with unit quantum efficiency. At 193 nm Melchior et al. (1997) have shown that C-Cl bond fission to give  $\text{CH}_3\text{CFC}l+\text{Cl}$  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).

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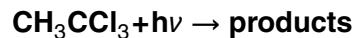
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### Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{CCl}_3 + h\nu \rightarrow \text{CH}_3\text{CCl}_2 + \text{Cl}$	335 (est)	360

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## Preferred Values

### Absorption cross-sections for CH<sub>3</sub>CCl<sub>3</sub> at 295 K and 210 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 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.

#### 5 **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-

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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  $\text{CH}_3\text{CCl}_2 + \text{Cl}$ .

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**CF<sub>3</sub>CHFCl+hν → products****Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF <sub>3</sub> CHFCl+hν → CF <sub>3</sub> CHF+Cl	335 (est)	360

**Preferred Values****Absorption cross-sections for CF<sub>3</sub>CHFCl at 298 K and 210 K**

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 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

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## 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  $\text{CF}_3\text{CHF}+\text{Cl}$ .

## 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.

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## Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_3\text{CHCl}_2 + h\nu \rightarrow \text{CF}_3\text{CHCl} + \text{Cl}$	335 (est)	360

## Preferred Values

Absorption cross-sections for  $\text{CF}_3\text{CHCl}_2$  at 298 K and 220 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 220 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 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

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## 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  $\text{CF}_3\text{CHCl} + \text{Cl}$ .

## 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.

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## Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_2\text{ClCFCl}_2 + h\nu$	$\rightarrow \text{CF}_2\text{ClCFCl} + \text{Cl}$ (1)	346 (est)	346
	$\rightarrow \text{CFCl}_2\text{CF}_2 + \text{Cl}$ (2)	346 (est)	346

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## Preferred Values

### Absorption cross-sections for $\text{CF}_2\text{ClCFCl}_2$ at 295 K and 210 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 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.

#### 5 **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  $\text{CF}_2\text{ClCFCl} + \text{Cl}$  or  $\text{CFCl}_2\text{CF}_2 + \text{Cl}$ .

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## 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.

- 5 Simon, P. C., Gillotay, D., Vanlaethem-Meuree, N., and Wisemberg, J.: Ann. Geophysicae, 6, 239, 1988.

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### Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_2\text{ClCF}_2\text{Cl} + h\nu \rightarrow \text{CF}_2\text{ClCF}_2 + \text{Cl}$	346 (est)	346

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## Preferred Values

### Absorption cross-sections for CF<sub>2</sub>CICF<sub>2</sub>Cl at 295 K and 210 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 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.

#### 5 **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

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dependence. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield  $\text{CF}_2\text{ClCF}_2 + \text{Cl}$ .

## References

5 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 Wisenberg, J.: Ann. Geophysicae, 6, 239, 1988.

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## Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ.mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_3\text{CF}_2\text{Cl} + h\nu \rightarrow \text{CF}_3\text{CF}_2 + \text{Cl}$	346	346

## Preferred Values

Absorption cross-sections for  $\text{CF}_3\text{CF}_2\text{Cl}$  at 295 K to 225 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
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		

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## 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  $\text{CF}_3\text{CF}_2 + \text{Cl}$ .

## 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.

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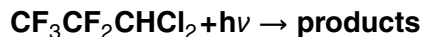
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### Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_3\text{CF}_2\text{CHCl}_2 + h\nu \rightarrow \text{CF}_3\text{CF}_2\text{CHCl} + \text{Cl}$	335 (est)	360

### Preferred Values

#### Absorption cross-sections for $\text{CF}_3\text{CF}_2\text{CHCl}_2$ at 298 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
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

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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  $\text{CF}_3\text{CF}_2\text{CHCl} + \text{Cl}$ .

## References

Braun, W., Fahr, A., Klein, R., Kurylo, M. J., and Huie, R. E.: J. Geophys. Res., 96, 13009, 1991.

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**CF<sub>2</sub>CICF<sub>2</sub>CHFCl+hν → products****Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF <sub>2</sub> CICF <sub>2</sub> CHFCl+hν → CF <sub>2</sub> CICF <sub>2</sub> CHF+Cl	335 (est)	360
→ CHFCICF <sub>2</sub> CF <sub>2</sub> +Cl	335 (est)	360

**Preferred Values****Absorption cross-sections for CF<sub>2</sub>CICF<sub>2</sub>CHFCl at 298 K**

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
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.,

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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:

$$\log_{10}\sigma = -17.714 - 2.175 \times 10^{-2} X - 1.484 \times 10^{-3} X^2 + 1.147 \times 10^{-5} X^3$$

5 where  $X = (\lambda - 160 \text{ nm})$

Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield  $\text{CF}_2\text{ClCF}_2\text{CHF} + \text{Cl}$  or  $\text{CHFClCF}_2\text{CF}_2 + \text{Cl}$ .

## References

10 Braun, W., Fahr, A., Klein, R., Kurylo, M. J., and Huie, R. E.: J. Geophys. Res., 96, 13009, 1991.

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**HC(O)Cl+h $\nu$  → products****Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HC(O)Cl+h $\nu$ → HCO+Cl	340 (est)	350

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## Preferred Values

Absorption cross-sections for HC(O)Cl at the band maxima  
(298 K, 1013 mbar of N<sub>2</sub>, spectral resolution 0.7 nm)

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
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

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## 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<sub>2</sub> 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.

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

## Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
C(O)FCl+h $\nu$ $\rightarrow$ FCO+Cl	(1)	396	302
$\rightarrow$ ClCO+F	(2)	485	247
$\rightarrow$ CO+F+Cl	(3)	517	231
$\rightarrow$ CFCl+O( $^3\text{P}$ )	(4)	707	169

## 5 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 $\pm$ 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<sub>2</sub> (and in the study of Hermann et al. (1994), also CO). Product formation was explained using only channels (1) and (3), because decomposition of

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CICO 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),  $FCO+FCO \rightarrow C(O)F_2+CO$ . 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

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
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

5 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<sup>-1</sup> intervals. Nölle et al. (1993) reported values over the wavelength range 200–260 nm and the temperature range 298–223 K. Their room

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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  $\Delta H^0(\text{C(O)FCl})[0\text{ K}] = -(397 \pm 15) \text{ kJ mol}^{-1}$  was obtained.

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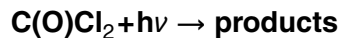
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### Primary photochemical transitions

Reaction		$\Delta H^\circ / \text{kJ mol}^{-1}$	$\lambda_{\text{threshold}} / \text{nm}$
$\text{C(O)Cl}_2 + h\nu \rightarrow \text{ClCO} + \text{Cl}$	(1)	320	374
$\rightarrow \text{CO} + 2\text{Cl}$	(2)	352	340
$\rightarrow \text{CCl}_2 + \text{O}(^3\text{P})$	(3)	699	171

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## Preferred Values

### Absorption cross-sections for C(O)Cl<sub>2</sub> at 298 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
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<sub>2</sub> at 298 K

5  $\Phi(1)=1.0$  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  $500 \text{ cm}^{-1}$

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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

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### Primary photochemical processes

Reaction	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\lambda_{\text{threshold}} / \text{nm}$
$\text{CF}_2\text{ClCHO} + h\nu \rightarrow \text{CF}_2\text{Cl} + \text{HCO}$ (1)		
$\rightarrow \text{CF}_2\text{ClCO} + \text{H}$ (2)		
$\rightarrow \text{CHF}_2\text{Cl} + \text{CO}$ (3)		

### 5 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

- 10 (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  $\sigma$  were given at 5 nm intervals at 298 K together with values of B in the expression  $\ln \sigma(T) = \ln \sigma(298 \text{ K}) + B(T - 298)$ .

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## Preferred Values

Absorption cross-sections for CF<sub>2</sub>CICHO at 298 K and their temperature dependence.

Wavelength	$10^{20}$ $\sigma(298\text{ K})/\text{cm}^2$	$10^4\text{ B/K}^{-1a)}$
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

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Wavelength	$10^{20}$ $\sigma(298\text{ K})/\text{cm}^2$	$10^4\text{ B/K}^{-1a)}$
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 $\text{CF}_2\text{ClCHO}$

No recommendation.

#### 5 **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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Rattigan, O. V., Wild, O., and Cox, R. A.: J. Photochem. Photobiol. A: Chem., 112, 1, 1998.

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### Primary photochemical processes

Reaction	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\lambda_{\text{threshold}} / \text{nm}$
$\text{CFCl}_2\text{CHO} + h\nu \rightarrow \text{CFCl}_2 + \text{HCO}$ (1)		
$\rightarrow \text{CFCl}_2\text{CO} + \text{H}$ (2)		
$\rightarrow \text{CHFCl}_2 + \text{CO}$ (3)		

### 5 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

- 10 (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  $\sigma$  were given at 5 nm intervals at 298 K together with values of B in the expression  $\ln \sigma(T) = \ln \sigma(298 \text{ K}) + B(T - 298)$ .

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## Preferred Values

### Absorption cross-sections for $\text{CFCl}_2\text{CHO}$ at 298 K and their temperature dependence

Wavelength	$10^{20}$ $\sigma(298\text{ K})/\text{cm}^2$	$10^4\text{ B/K}^{-1a)}$
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

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Wavelength	$10^{20}$ $\sigma(298\text{ K})/\text{cm}^2$	$10^4\text{ B/K}^{-1a)}$
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

<sup>a)</sup>  $\ln \sigma(T) = \ln \sigma(298\text{ K}) + B(T - 298)$

### Quantum yield for $\text{CFCl}_2\text{CHO}$

No recommendation.

#### 5 **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

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shows a similar absorption spectrum, photodissociation is expected to be predominantly by channel (1).

## References

- 5 Rattigan, O. V., Wild, O., and Cox, R. A.: J. Photochem. Photobiol. A: Chem., 112, 1, 1998.

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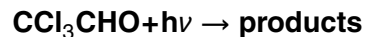
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### Primary photochemical processes

Reaction	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\lambda_{\text{threshold}} / \text{nm}$
$\text{CCl}_3\text{CHO} + h\nu \rightarrow \text{CCl}_3 + \text{HCO}$ (1)		
$\rightarrow \text{CCl}_3\text{CO} + \text{H}$ (2)		
$\rightarrow \text{CHCl}_3 + \text{CO}$ (3)		
$\rightarrow \text{CCl}_2\text{CHO} + \text{Cl}$ (4)		

### 5 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)

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## Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi[\text{H}]=0.04\pm 0.005$	193	Talukdar et al., 2001	(d)
$\Phi[\text{O}(^3\text{P})] < 0.02$	248		
$\Phi[\text{H}] < 0.01$	248		
$\Phi[\text{O}(^3\text{P})] < 0.01$	308		
$\Phi[\text{H}] < 0.002$	308		
$\Phi[\text{Cl}]=1.3\pm 0.3$	308		
$\Phi[-\text{CCl}_3\text{CHO}]=1.00\pm 0.05$	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  $\sigma$  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  $\sigma$  were given at 5 nm intervals at 298 K together with the values of B in the expression  $\ln \sigma(T)=\ln \sigma(298 \text{ K})+B(T-298)$ .
- (c) Absolute absorption cross-sections were measured using a diode array spectrometer over the temperature range 240–360 K. Values of  $\sigma$  were listed at 298 K at 2 nm intervals, together with the values of B in the expression  $\ln \sigma(T)=\ln \sigma(298 \text{ K})+B(T-298)$ .

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(d) Determined from pulsed laser photolysis of  $\text{CCl}_3\text{CHO}$  with detection of H,  $\text{O}(^3\text{P})$  and Cl atoms by resonance fluorescence. Experiments were carried out at  $298 \pm 2$  K, and the H,  $\text{O}(^3\text{P})$  and Cl atom signals were placed on an absolute basis by use of photolysis of HBr (193 nm) or  $\text{CH}_3\text{SH}$  (248 and 308 nm) as reference compounds for H atom formation, photolysis of  $\text{O}_3$  in the presence of  $\text{N}_2$  at 248 and 308 nm as a reference compound for production of  $\text{O}(^3\text{P})$  atoms, and photolysis of  $\text{Cl}_2$  at 308 nm as a reference compound for production of Cl atoms. Because Cl atoms react with  $\text{CCl}_3\text{CHO}$ , their yield was obtained by extrapolation to zero time. Cl atom formation was shown to be a primary process. Photolysis of  $\text{CCl}_3\text{CHO}$  at 248 nm in the presence of  $\text{O}_2$  led to the formation of CO and  $\text{C}(\text{O})\text{Cl}_2$ , with no formation of  $\text{CHCl}_3$  (thereby ruling out the occurrence of channel (3) at 248 nm).

(e) Determined from the photolysis of  $\text{CCl}_3\text{CHO}$  in the  $\sim 200 \text{ m}^3$  volume EUPHORE chamber under natural sunlight conditions at  $298 \pm 5$  K. Cyclohexane was added to scavenge Cl atoms and  $\text{SF}_6$  was added to monitor dilution and loss through leakage.  $\text{CCl}_3\text{CHO}$  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  $\text{CCl}_3\text{CHO}$ , corrected for dilution, were compared to the calculated decay rates for a photodissociation quantum yield of 1.00.

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### Absorption cross-sections of CCl<sub>3</sub>CHO at 298 K and their temperature dependence

Wavelength	$10^{20}$ $\sigma(298\text{ K})/\text{cm}^2$	$10^4\text{ B/K}^{-1a}$
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

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Wavelength	$10^{20}$ $\sigma(298\text{ K})/\text{cm}^2$	$10^4\text{ B/K}^{-1a}$
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

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Wavelength	$10^{20}$ $\sigma(298\text{ K})/\text{cm}^2$	$10^4\text{ B/K}^{-1a)}$
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

$a) \ln \sigma(T) = \ln \sigma(298\text{ K}) + B(T-298)$

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## Quantum yield for CCl<sub>3</sub>CHO

$\Phi(4)=1.0$  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<sub>2</sub>, CO and Cl atoms from the photolysis of CCl<sub>3</sub>CHO at 290–400 nm, with molar yields of  $0.83\pm 0.04$ ,  $1.01\pm 0.05$  and  $1.18\pm 0.06$ , 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<sub>2</sub>CHO [channel (4)].

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**CF<sub>3</sub>C(O)Cl+hν → products****Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF <sub>3</sub> C(O)Cl+hν → CF <sub>3</sub> +ClCO (1)		
→ CF <sub>3</sub> CO+Cl (2)		

5 **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)

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## 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 ( $\sigma=6.87\times 10^{-19}\text{ cm}^2\text{ molecule}^{-1}$ ), and the second at  $\lambda<200\text{ nm}$ . There is significant absorption at wavelengths  $>300\text{ nm}$ , where the cross-sections become increasingly temperature dependent. The estimated overall errors in the values of  $\sigma$  were  $\pm 3\%$  over the wavelength range 200–310 nm, increasing to  $\pm 20\%$  for longer wavelengths where the cross-sections (and hence absorptions) are low. Values of  $\sigma$  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  $>300\text{ nm}$  (up to 20% error at 330 nm):

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	$\lambda=200\text{--}220\text{ nm}$	$\lambda=218\text{--}330\text{ nm}$
$A_0$	$-2.0111750 \times 10^4$	$-8.8912918 \times 10^1$
$A_1$	$3.1757333 \times 10^2$	$9.6418661 \times 10^{-1}$
$A_2$	$-2.5671017$	$-5.4370794 \times 10^{-3}$
$A_3$	$7.8520098 \times 10^{-3}$	$1.4975946 \times 10^{-5}$
$A_4$	$-8.9707718 \times 10^{-6}$	$-1.6768324 \times 10^{-7}$
$B_0$	$3.0306320 \times 10^2$	$3.7950580$
$B_1$	$-5.8082356$	$-5.9114731 \times 10^{-2}$
$B_2$	$4.1715164 \times 10^{-2}$	$3.4406419 \times 10^{-4}$
$B_3$	$-1.3306565 \times 10^{-4}$	$-8.8699856 \times 10^{-7}$
$B_4$	$1.5906451 \times 10^{-7}$	$8.5483894 \times 10^{-10}$

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(b) Average of measurements of the overall loss of  $\text{CF}_3\text{C}(\text{O})\text{Cl}$  during photolysis in  $\text{N}_2$ . Measurements of the photodissociation quantum yield of  $\text{CF}_3\text{C}(\text{O})\text{Cl}$  in air at total pressures of 67–1013 mbar showed no effect of total pressure or of the presence of  $\text{O}_2$ .

(c) Pulsed laser photolysis of  $\text{CF}_3\text{C}(\text{O})\text{Cl}-\text{C}_2\text{H}_6-\text{O}_2-\text{N}_2$  mixtures at a total pressure of 160 mbar, with detection of  $\text{CF}_3\text{O}_2$  radicals by time-resolved UV spectroscopy and of HCl by IR spectroscopy.  $\text{CF}_3\text{O}_2$  radicals were formed from  $\text{CF}_3$  radicals and HCl was formed from  $\text{Cl}+\text{C}_2\text{H}_6 \rightarrow \text{HCl}+\text{C}_2\text{H}_5$ . The system was calibrated by photolysis of  $\text{CH}_3\text{Cl}$  at 193 nm and of  $\text{Cl}_2$  at 248 nm instead of  $\text{CF}_3\text{C}(\text{O})\text{Cl}$ , with the assumption that the photodissociation quantum yields of  $\text{CH}_3\text{Cl}$  and  $\text{Cl}_2$  are unity.

(d) Quantum yields derived from the amounts of  $\text{C}_2\text{F}_6$  and  $\text{CF}_3\text{Cl}$  formed from irradiating  $\text{CF}_3\text{C}(\text{O})\text{Cl}$  at 254 and 280 nm (high pressure mercury arc-monochromator combination). Actinometry was performed with potassium ferrioxalate solution. It was observed that  $(2[\text{C}_2\text{F}_6]+[\text{CF}_3\text{Cl}])/[\text{CO}]=0.99\pm 0.05$ , consistent with formation of  $\text{CF}_3$  radicals, Cl atoms and CO followed by the combination reactions  $\text{CF}_3+\text{CF}_3 \rightarrow \text{C}_2\text{F}_6$  and  $\text{CF}_3+\text{Cl} \rightarrow \text{CF}_3\text{Cl}$ . Hence  $\Phi(-\text{CF}_3\text{C}(\text{O})\text{Cl})=2\Phi(\text{C}_2\text{F}_6)+\Phi(\text{CF}_3\text{Cl})$ .

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## Preferred Values

### Absorption cross-sections of CF<sub>3</sub>COCl at 298 K and their temperature dependence

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 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

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$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 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

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$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 223 K
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  $\text{CF}_3\text{COCl}$**

$\Phi_1 + \Phi_2 = 1.0$  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), Maricq 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<sub>3</sub>CO radical dissociating totally at 193 nm and ~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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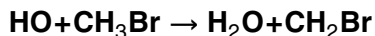
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## Appendix 3: BrO<sub>x</sub> Reactions

### IV.A3.243



$$\Delta H^\circ = -71.9 \text{ kJ mol}^{-1}$$

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#### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.5 \pm 0.8) \times 10^{-14}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$7.93 \times 10^{-13} \exp[-(889 \pm 59)/T]$	244–350	Davis et al., 1976	FP-RF
$(4.14 \pm 0.43) \times 10^{-14}$	298		
$2.35 \times 10^{-12} \exp[-(1300 \pm 150)/T]$	233–379	Mellouki et al., 1992	PLP-LIF
$(2.96 \pm 0.36) \times 10^{-14}$	298		
$5.79 \times 10^{-12} \exp[-(1560 \pm 150)/T]$	250–400	Zhang et al., 1992	FP-RF
$(3.08 \pm 0.47) \times 10^{-14}$	298		
$1.86 \times 10^{-12} \exp[-(1230 \pm 150)/T]$	248–390	Chichinin et al., 1994	DF-EPR
$(3.03 \pm 0.45) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$5.43 \times 10^{-18} T^2 \exp[-(812 \pm 46)/T]$	298–360	Hsu and Demore, 1994	RR (a)
$3.16 \times 10^{-14}$	298		

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## Comments

(a) HO radicals were generated from the UV photolysis of O<sub>3</sub> in the presence of water vapor, in O<sub>3</sub>-H<sub>2</sub>O-CH<sub>3</sub>Br-CH<sub>3</sub>CHF<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures. The concentrations of CH<sub>3</sub>Br and CH<sub>3</sub>CHF<sub>2</sub> were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO}+\text{CH}_3\text{Br})/k(\text{HO}+\text{CH}_3\text{CHF}_2)=(1.94 \pm 0.28) \exp[-(232 \pm 46)/T]$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO}+\text{CH}_3\text{CHF}_2)=2.80 \times 10^{-18} T^2 \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

## Preferred Values

$k=2.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k=1.7 \times 10^{-12} \exp(-1215/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240–300 K.

## Reliability

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

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

## 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

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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  $k=3.44 \times 10^{-18} T^2 \exp(-687/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 233–400 K. The preferred Arrhenius expression,  $k=A \exp(-B/T)$ , is centered at 265 K and is derived from three parameter expression with  $A=C e^2 T^2$  and  $B=D+2T$ .

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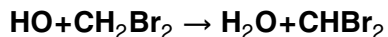
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$$\Delta H^\circ = -79.6 \text{ kJ mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.91 \times 10^{-12} \exp[-(840 \pm 100)/T]$	243–380	Mellouki et al., 1992	PLP-LIF
$(1.13 \pm 0.15) \times 10^{-13}$	298		
$1.51 \times 10^{-12} \exp[-(720 \pm 60)/T]$	288–368	Zhang et al., 1997	DF-RF
$(1.33 \pm 0.14) \times 10^{-13}$			
<i>Relative Rate Coefficients</i>			
$(9.7 \pm 0.6) \times 10^{-14}$	298	Orlando et al., 1996	RR (a)
$1.51 \times 10^{-12} \exp[-(715 \pm 39)/T]$	293–375	DeMore, 1996	RR (b)
$1.37 \times 10^{-13}$	298		

**Comments**

(a) HO radicals were generated by the photolysis of  $\text{O}_3$  in the presence of  $\text{H}_2\text{O}$ , and acetone was used as the reference compound.  $\text{CH}_2\text{Br}_2$  and acetone were monitored by FTIR spectroscopy, and a rate coefficient ratio of  $k(\text{HO} + \text{CH}_2\text{Br}_2)/k(\text{HO} + \text{acetone}) = 0.54 \pm 0.03$  was determined. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of

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$k(\text{HO}+\text{acetone})=1.8\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of  $\text{O}_3$  at 254 nm in the presence of  $\text{H}_2\text{O}$ , and  $\text{CH}_2\text{Cl}_2$  was used as the reference compound.  $\text{CH}_2\text{Br}_2$  and  $\text{CH}_2\text{Cl}_2$  were monitored by FTIR spectroscopy, and a rate coefficient ratio of  $k(\text{HO}+\text{CH}_2\text{Br}_2)/k(\text{HO}+\text{CH}_2\text{Cl}_2)=0.84\text{ exp}[(145\pm 39)/T]$  was determined. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO}+\text{CH}_2\text{Cl}_2)=1.8\times 10^{-12}\text{ exp}(-860/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

$k=1.1\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

$k=1.5\times 10^{-12}\text{ exp}(-775/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the temperature range 240–300 K.

### Reliability

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

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

### 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  $9.7\times 10^{-14}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  to  $1.43\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ . 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  $k = 2.86 \times 10^{-18} T^2 \exp(-246/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 243–380 K. The preferred Arrhenius expression,  $k = A \exp(B/T)$ , is centered at 265 K and is derived from the three-parameter expression with  $A = C e^2 T^2$  and  $B = D + 2T$ .

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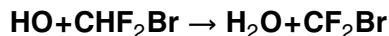
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.4 \times 10^{-13} \exp[-(1050 \pm 400)/T]$ $(1.3 \pm 0.3) \times 10^{-14}$	275–420 298	Brown et al., 1990	DF-RF
$7.4 \times 10^{-13} \exp[-(1300 \pm 100)/T]$ $(1.06 \pm 0.08) \times 10^{-14}$	233–432 298	Talukdar et al., 1991	PLP-LIF/DF-LMR
$9.3 \times 10^{-13} \exp[-(1326 \pm 33)/T]$ $(1.10 \pm 0.09) \times 10^{-14}$	298–460 298	Orkin and Khamaganov, 1993	DF-EPR
<i>Relative Rate Coefficients</i>			
$6.11 \times 10^{-21} T^{2.82} \exp[-(527 \pm 31)/T]$ $9.9 \times 10^{-15}$	283–368 298	Hsu and DeMore, 1995	RR (a)

5 **Comments**

(a) HO radicals were generated by the UV photolysis of O<sub>3</sub> in the presence of water vapor in O<sub>3</sub>-H<sub>2</sub>O-CHF<sub>2</sub>Br-CH<sub>4</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures. The concentrations of CHF<sub>2</sub>Br and CH<sub>4</sub> were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CHF}_2\text{Br}) / k(\text{HO} + \text{CH}_4) = (0.33 \pm 0.03) \exp[(460 \pm 31)/T]$  is placed on an absolute basis by using a rate coefficient of  $k(\text{HO} + \text{CH}_4) = 1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

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## Preferred Values

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

$k = 7.9 \times 10^{-13} \exp(-1300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230–360 K.

### 5 **Reliability**

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

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

### **Comments on Preferred Values**

10 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.

15 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  
20 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.

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Hsu, K.-J. and DeMore, W. B.: J. Phys. Chem., 99, 1235, 1995.

5 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.

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HO+CF<sub>3</sub>Br → products

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<1.2 \times 10^{-16}$	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		

## 5 Preferred Values

$k < 6.0 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k < 1.0 \times 10^{-12} \exp(-3600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–460 K.

**Comments on Preferred Values**

10 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  $\sim 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The lower limit for *E/R* was estimated to be  $>3600 \text{ K}$  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  
 15 obtained using these parameters.

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HO+CF<sub>2</sub>ClBr → products

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<1 \times 10^{-15}$	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

## 5 Preferred Values

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

$k < 1 \times 10^{-12} \exp(-3450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–380 K.

**Comments on Preferred Values**

10 The studies of Clyne and Holt (1979) and Burkholder et al. (1991) both observed no reaction of HO radicals with CF<sub>2</sub>ClBr. The preferred upper limit Arrhenius expression is obtained from an assumed Arrhenius pre-exponential factor of  $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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

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rate coefficient which is consistent with the room temperature data of Clyne and Holt (1979) and Burkholder et al. (1991).

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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.

5 Clyne, M. A. A. and Holt, P. M.: J. Chem. Soc. Faraday Trans., 2, 75, 569, 1979.

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HO+CF<sub>2</sub>Br<sub>2</sub> → products

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<4.0 \times 10^{-16}$	384–424	Burkholder et al., 1991	DF-LMR/PLP-LIF
$<5.0 \times 10^{-16}$	298		

## 5 Preferred Values

$k < 5.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k < 1.0 \times 10^{-12} \exp(-2200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–460 K.

**Comments on Preferred Values**

10 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  $k < 4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  measured at 384 and 424 K. The *A*-factor for the reaction was estimated to be  $\sim 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The lower limit for *E/R* was estimated to be  $>2200 \text{ K}$  based on the upper limit value of the rate coefficient

15 determined by Burkholder et al. (1991) at 298 K.

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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.

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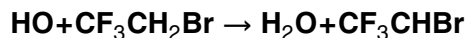
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**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$8.5 \times 10^{-13} \exp[-(1113 \pm 35)/T]$ $(2.05 \pm 0.16) \times 10^{-14}$	298–460 298	Orkin and Khamaganov, 1993	DF-EPR
$1.39 \times 10^{-12} \exp[-(1350 \pm 195)/T]$ $(1.45 \pm 0.13) \times 10^{-14}$	280–353 294	Nelson et al., 1993	DF-LIF

5 **Preferred Values**

$k = 1.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.4 \times 10^{-12} \exp(-1340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 280–460 K.

**Reliability**

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

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

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## 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

5 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.

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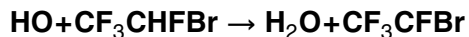
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**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.13 \times 10^{-12} \exp[-(1250 \pm 364)/T]$ $(1.7 \pm 0.3) \times 10^{-14}$	279–423 298	Brown et al., 1990	DF-RF
$7.2 \times 10^{-13} \exp[-(1111 \pm 32)/T]$ $(1.75 \pm 0.17) \times 10^{-14}$	298–460 298	Orkin and Khamaganov, 1993	DF-EPR

5 **Preferred Values**

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

$k = 8.1 \times 10^{-13} \exp(-1155/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270–460 K.

**Reliability**

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

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

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## 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.

### 5 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.

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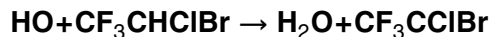
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**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.0 \pm 0.4) \times 10^{-14}$	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		

5 **Preferred Values**

$k = 4.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.2 \times 10^{-12} \exp(-970/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290–460 K.

**Reliability**

$\Delta \log k = \pm 0.20$  at 298 K.

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

**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-

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squares analysis of the rate coefficients of Orkin and Khamaganov (1993) leads to the preferred Arrhenius expression.

## References

- 5 Brown, A. C., Canosa-Mas, C. E., Parr, A. D., Pierce, J. M. T., and Wayne, R. P.: Nature, 341, 635, 1989.
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## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<1.5 \times 10^{-16}$	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		

## 5 Preferred Values

$k < 6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k < 1 \times 10^{-12} \exp(-3600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–460 K.

**Comments on Preferred Values**

10 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  $\sim 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The lower limit for *E*/*R* was estimated to be  $>3600 \text{ K}$  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.

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Orkin, V. L. and Khamaganov, V. G.: J. Atmos. Chem., 16, 169, 1993.

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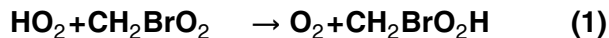
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#### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.7 \pm 3.8) \times 10^{-12}$	298	Villeneuve and Lesclaux, 1995	FP-UVA (a)
<i>Branching Ratios</i>			
$k_1/k \geq 0.85$	297	Chen et al., 1995	UVP-FTIR (b)
$k_2/k \leq 0.15$			

#### 5 Comments

(a) Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Br}-\text{CH}_3\text{OH}-\text{O}_2-\text{N}_2$  mixtures at a pressure of 1013 mbar. Decays in transient absorptions (with contributions from  $\text{CH}_2\text{BrO}_2$  and  $\text{HO}_2$ ) were recorded in the wavelength range 250 nm to 280 nm.  $k$  derived from simulations of the decay traces using an explicit reaction mechanism.

10 (b)  $\text{CH}_2\text{BrO}_2$  and  $\text{HO}_2$  radicals were generated from the steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Br}-\text{H}_2$ -air mixtures at 933 mbar. FTIR spectroscopic analysis identified  $\text{CH}_2\text{BrO}_2\text{H}$  and  $\text{HC(O)Br}$  as carbon-containing primary products. The cited branching ratios were derived by taking account of secondary reactions in the system, and the possibility that  $\text{HC(O)Br}$  is formed from the in-situ oxidation of  $\text{CH}_2\text{BrO}_2\text{H}$ .

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## Preferred Values

$k=6.7\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

$k_1/k=1.0$  at 298 K.

## Reliability

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

$\Delta (k_1/k)=_{-0.15}^{+0.00}$  at 298 K.

## Comments on Preferred Values

10 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 (Villeneuve and Lesclaux, 1995),  $k$  is indistinguishable from that recommended for the reactions of  $\text{HO}_2$  with  $\text{CH}_3\text{O}_2$  and  $\text{CH}_2\text{ClO}_2$  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  $\text{CH}_2\text{ClO}_2$ , for which formation of  $\text{HC(O)Cl}$ ,  $\text{H}_2\text{O}$  and  $\text{O}_2$  is the major pathway. Con-  
15 firmatory product studies are also required.

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Chen, J., Catoire, V., and Niki, H.: Chem. Phys. Lett., 245, 519, 1995.

Villeneuve, E. and Lesclaux, R.: Chem. Phys. Lett., 236, 376, 1995.

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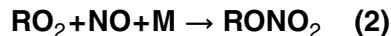
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(254: R=CH<sub>2</sub>Br; 255: R=CHBr<sub>2</sub>)

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
R=CH <sub>2</sub> Br (1.07±0.11)×10 <sup>-11</sup>	295	Sehested et al., 1993	PR-AS (a)
R=CHBr <sub>2</sub> (1.74±0.16)×10 <sup>-11</sup>	296	Bayes et al., 2005	PLP-RF (b)

### Comments

(a)  $k$  determined from  $+d[\text{NO}_2]/dt$  at a total pressure of 1 bar.

(b) Photolysis of CHBr<sub>3</sub> in the presence of O<sub>2</sub> 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<sub>2</sub>O.  $k$  was independent of pressure in the studied range.

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## Preferred Values



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

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

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

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

## 10 *Comments on Preferred Values*



The preferred values are the rounded-off rate coefficients determined by Sehested et al. (1993).

15



The preferred value is the rounded-off rate coefficient determined by Bayes et al. (2005).

## References

20

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.

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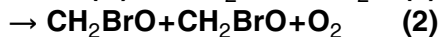
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#### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = (3.26 \pm 0.31) \times 10^{-11}$	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)
<i>Branching Ratios</i>			
$k_2/k \approx 1.0$	298	Nielsen et al., 1991	UVP-FTIR (d)
$k_2/k \approx 1.0$	297	Chen et al., 1995	UVP-FTIR (e)

#### 5 Comments

(a)  $k_{\text{obs}}$  is based on the measured overall second-order decay of  $\text{CH}_2\text{BrO}_2$ , defined by  $-\text{d}[\text{CH}_2\text{BrO}_2]/\text{dt} = 2k_{\text{obs}}[\text{CH}_2\text{BrO}_2]^2$ . Br atoms and  $\text{HO}_2$  radicals formed from the subsequent chemistry of  $\text{CH}_2\text{BrO}$  (formed from channel (2)) are expected to lead to secondary removal of  $\text{CH}_2\text{BrO}_2$ , such that  $k_{\text{obs}}$  represents an upper limit for the true value of  $k$ .

(b) Pulse radiolysis study of  $\text{CH}_3\text{Br}-\text{O}_2-\text{SF}_6$  mixtures with  $\text{CH}_2\text{BrO}_2$  radicals being monitored by UV absorption, with  $\sigma_{250\text{nm}} = (7.20 \pm 0.83) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . The derived value of  $k_{\text{obs}}$  was found to be independent of wavelength over the range 250–310 nm and of pressure over the range 150–1000 mbar of  $\text{SF}_6$ .

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(c) Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Br}-\text{O}_2-\text{N}_2$  mixtures at a pressure of 1013 mbar, with  $\text{CH}_2\text{BrO}_2$  radicals being monitored by UV absorption, with  $\sigma_{250\text{ nm}} = (3.35 \pm 0.10) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$ . 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)  $\text{CH}_2\text{BrO}_2$  radicals were generated from the steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Br}$ -air mixtures. Two major carbon-containing products, CO and  $\text{HC(O)Br}$ , were observed by FTIR spectroscopic analysis.  $\text{HC(O)Br}$  was believed to arise from the reaction of  $\text{CH}_2\text{BrO}$  with  $\text{O}_2$ .

(e)  $\text{CH}_2\text{BrO}_2$  radicals were generated from the steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Br}$ -air mixtures at 930 mbar. FTIR spectroscopic analysis identified  $\text{CH}_2\text{O}$  as the major carbon-containing primary product, suggesting  $\text{CH}_2\text{BrO}$  (formed from channel (2)) predominantly decomposes by Br atom elimination. Lower yields of  $\text{HC(O)Br}$  were observed, but  $\text{CH}_2\text{BrOH}$  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

$\Delta(k_2/k) = {}_{-0.1}^{+0.0}$  at 298 K.

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## 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  $\text{CH}_2\text{BrOH}$  (which would be formed by channel (1)) was obtained. Observation of  $\text{CH}_2\text{O}$  as the major primary product was also consistent with the dominance of channel (2), followed by decomposition of  $\text{CH}_2\text{BrO}$  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  $\text{CH}_2\text{BrO}_2$  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  $\text{CH}_2\text{BrO}_2$ , the mechanism used to extract  $k$  from the observed decay profiles assumed secondary removal of  $\text{CH}_2\text{BrO}_2$  by reaction with  $\text{HO}_2$  generated from the exclusive reaction of  $\text{CH}_2\text{BrO}$  with  $\text{O}_2$ . It is possible that the actual formation of Br atoms leads to a similar degree of secondary removal of  $\text{CH}_2\text{BrO}_2$ , 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.

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Villenave, E. and Lesclaux, R.: Chem. Phys. Lett., 236, 376, 1995.

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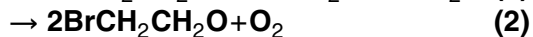
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#### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = (6.2 \pm 1.2) \times 10^{-12}$	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		
<i>Branching Ratios</i>			
$k_1/k = 0.43$	296	Yarwood et al., 1992	UV-P-FTIR (d)
$k_2/k = 0.57$			

#### 5 Comments

(a)  $k_{\text{obs}}$  is based on the measured overall second-order decay of  $\text{CH}_2\text{BrCH}_2\text{O}_2$ , defined by  $-\text{d}[\text{CH}_2\text{BrCH}_2\text{O}_2]/\text{dt} = 2k_{\text{obs}} [\text{CH}_2\text{BrCH}_2\text{O}_2]^2$ . As described in detail by Lesclaux (1997),  $\text{HO}_2$  radicals formed from the subsequent chemistry of  $\text{CH}_2\text{BrCH}_2\text{O}$  (formed from channel (2)) are expected to lead to secondary removal of  $\text{CH}_2\text{BrCH}_2\text{O}_2$ . The true value of  $k$  is expected to fall in the range  $k_{\text{obs}}/(1+\alpha) < k < k_{\text{obs}}$ , where  $\alpha = k_2/k$ .

(b) Molecular modulation study of the photolysis of  $\text{Br}_2$  in the presence of  $\text{C}_2\text{H}_4\text{-O}_2\text{-N}_2$  mixtures at total pressures up to 800 mbar. Modulated waveforms for the

formation and removal of  $\text{CH}_2\text{BrCH}_2\text{O}_2$  radicals were monitored by absorption at 270 nm, i.e. where  $\text{HO}_2$  does not absorb.

(c) Flash photolysis of  $\text{Br}_2$  in the presence of  $\text{C}_2\text{H}_4\text{-O}_2\text{-N}_2$  mixtures at a pressure of 1013 mbar. Decays in transient absorption signals (with contributions from  $\text{CH}_2\text{BrCH}_2\text{O}_2$  and  $\text{HO}_2$ ) 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  $\text{Br}_2$  in the presence of  $\text{C}_2\text{H}_4\text{-O}_2\text{-N}_2$  mixtures at 933 mbar total pressure, with FTIR spectroscopic determination of products. The major products observed were  $\text{BrCH}_2\text{CHO}$ ,  $\text{BrCH}_2\text{CH}_2\text{OH}$ , and  $\text{BrCH}_2\text{CH}_2\text{OOH}$ . The branching ratio,  $k_2/k_1=1.35 \pm 0.07$ , was determined from the yields of  $\text{BrCH}_2\text{CHO}$  and  $\text{BrCH}_2\text{CH}_2\text{OH}$  relative to the loss of  $\text{C}_2\text{H}_4$ .

### Preferred Values

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

$k=6.0 \times 10^{-14} \exp(1250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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.

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

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

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## 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  $k_{\text{obs}}$  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  $\text{CH}_2\text{ClCH}_2\text{O}_2$ , both showing an enhancement of a factor of ca. 50 compared with the self-reaction rate coefficient for the unsubstituted analogue,  $\text{C}_2\text{H}_5\text{O}_2$ .

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- Crowley, J. N. and Moortgat, G. K.: J. Chem. Soc. Faraday Trans., 88, 2437, 1992.  
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Yarwood, G., Peng, N. and Niki, H.: Int. J. Chem. Kinet., 24, 369, 1992.

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$$\Delta H^\circ(1) = -3.5 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = +52.4 \text{ kJ mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.7 \pm 0.6) \times 10^{-12}$	298	Aranda et al., 1997	DF-MS/LIF (a)
<i>Branching Ratios</i>			
$k_3/k = 0.8 \pm 0.2$	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<sub>3</sub>O<sub>2</sub> were formed in the reactions Br+O<sub>3</sub>, and F+CH<sub>4</sub> in the presence of O<sub>2</sub>, respectively, and monitored by MS as their parent ions. The experiments were conducted under pseudo first-order conditions, with BrO in excess of CH<sub>3</sub>O<sub>2</sub>. The products observed were HOBr (MS) and CH<sub>3</sub>O (LIF). The CH<sub>3</sub>O profile was modeled by taking into account its presence as impurity in the CH<sub>3</sub>O<sub>2</sub> source, and its reaction with BrO.

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## Preferred Values

$k=5.7\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 298 K.

$k_1/k=0.25$  at 298 K.

$k_3/k=0.75$  at 298 K.

## 5 *Reliability*

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

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

$\Delta (k_3/k)=\begin{matrix} +0.25 \\ -0.4 \end{matrix}$  at 298 K.

## *Comments on Preferred Values*

10 The preferred value of  $k(298\text{ K})$  is taken from the sole study of this reaction with expanded error limits. The branching ratio to HOBr formation (reaction 3) was determined as  $(0.8\pm 0.2)$ , and that to  $\text{CH}_3\text{O}$  formation as  $(0.3\pm 0.1)$ . 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  $\text{CH}_3\text{OBr}$  and HBr. We also note that channel 15 (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  $\text{CH}_3\text{O}$  signal was achieved by modeling the  $\text{CH}_3\text{O}_2$  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  $\text{CH}_3\text{O}$  with the excess BrO (Aranda et al., 1998). Theoretical studies (Guha 20

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and Francisco, 2003) have been unable to reproduce the experimentally derived reaction mechanism and suggest that HOObBr and HCHO are formed via rearrangement of a CH<sub>3</sub>OOObBr association complex. Further experiments to examine temperature dependent kinetics and product formation in this reaction are desirable.

## 5 References

Aranda, A., Le Bras, G., La Verdet, G., and Poulet, G.: Geophys. Res. Lett., 24, 2745, 1997.

Aranda, A., Daële, V., Le Bras, G., and Poulet, G.: Int. J. Chem. Kinetic., 30, 249, 1998.

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**CH<sub>3</sub>Br+hν → products****Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH <sub>3</sub> Br+hν → CH <sub>3</sub> +Br	296	404

5 **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
$\Phi(\text{Br})=1.01\pm 0.16$	248	Talukdar et al., 1992	(b)
$\Phi(\text{Br})=1.10\pm 0.20$	222		
$\Phi(\text{Br})=1.05\pm 0.11$	193		
$\Phi(\text{H})=0.002\pm 0.001$	193		

**Comments**

- 10 (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 16992

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of 0.015 nm. Pressures of CH<sub>3</sub>Br 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.

- 5 (b) Pulsed laser photolysis of CH<sub>3</sub>Br-N<sub>2</sub> or He mixtures and detection of Br(<sup>2</sup>P<sub>3/2</sub>) by resonance fluorescence. A small amount of H<sub>2</sub> was added to ensure rapid quenching of the Br(<sup>2</sup>P<sub>1/2</sub>) also produced. The Br(<sup>2</sup>P<sub>3/2</sub>) 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
- 10 photolyses.

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## Preferred Values

### Absorption cross-sections of CH<sub>3</sub>Br at 295 K and 210 K.

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 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  $\sigma$  over the range 210–295 K

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## 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.

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**CF<sub>3</sub>Br+hν → products****Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF <sub>3</sub> Br+hν → CF <sub>3</sub> +Br	296	404

5 **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**

- 10 (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

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of 0.015 nm. Pressures of CF<sub>3</sub>Br 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 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) Pulsed laser photolysis of CF<sub>3</sub>Br-N<sub>2</sub> mixtures and detection of Br(<sup>2</sup>P<sub>3/2</sub>) by resonance fluorescence. A small amount of H<sub>2</sub> was added to ensure rapid quenching of the Br(<sup>2</sup>P<sub>1/2</sub>) also produced. The Br(<sup>2</sup>P<sub>3/2</sub>) measurements were calibrated by CH<sub>3</sub>Br photolysis at the same wavelength for which a quantum yield of unity was assumed.

## Preferred Values

### Absorption cross-sections of CF<sub>3</sub>Br at 295 K and 210 K.

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 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	

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## 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  $\sigma$  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

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the C-Br bond to give  $\text{CF}_3 + \text{Br}$ . Studies of the dynamics of Photodissociation at 234 nm show that 80% of the Br atoms are produced in the  $^2\text{P}_{1/2}$  excited state (Kim et al., 2001).  $\text{CF}_3\text{Br}$  has no apparent tropospheric chemistry loss mechanism (Burkholder et al., 1991) and is estimated to have a tropospheric lifetime against direct solar photoexcitation of greater than 1000 years (Molina et al., 1982).

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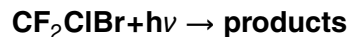
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### Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_2\text{ClBr} + h\nu \rightarrow \text{CF}_2 + \text{ClBr}$ (1)	296	445
$\rightarrow \text{CF}_2\text{Cl} + \text{Br}$ (2)	271	441
$\rightarrow \text{CF}_2\text{Br} + \text{Cl}$ (3)	348 (est)	344
$\rightarrow \text{CF}_2 + \text{Cl} + \text{Br}$ (4)	488	245

### 5 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)

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## Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\Phi(\text{Cl})=1.03\pm 0.14$	193	Talukdar et al., 1996	(d)
$\Phi(\text{Br})=1.04\pm 0.14$	193		
$\Phi(\text{CF}_2)=0.9\pm 0.2$	193		
$\Phi(\text{Cl})=0.27\pm 0.04$	222		
$\Phi(\text{Br})=0.86\pm 0.04$	222		
$\Phi(\text{Cl})=0.18\pm 0.03$	248		
$\Phi(\text{Br})=0.75\pm 0.12$	248	Yokoyama et al., 2001	(e)
$\Phi(3)=0.29\pm 0.03$	157.6		
$\Phi(2)=0.46\pm 0.05$	157.6		
$\Phi(4)=0.25\pm 0.05$			
$\Phi(3)=0.24$	234	Lee and Yung, 2001	(f)
$\Phi(2)=0.96$	234		

## Comments

5 (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  $\text{CF}_2\text{ClBr}$  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.

10 (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

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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  $\text{CF}_2\text{ClBr}$  and a reference compound in “back-to-back” experiments. For  $\Phi(\text{Cl})$  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 193 nm.  $\text{CH}_3\text{Br}$  and  $\text{C}_2\text{F}_4$  were used as reference compounds for measuring the yields of Br and  $\text{CF}_2$  respectively.  $[\text{Cl}]$  and  $[\text{Br}]$  were monitored by RF and  $[\text{CF}_2]$  by long path absorption.  $[\text{CF}_2\text{ClBr}]$  and  $[\text{HCl}]$  were determined by UV absorption and  $[\text{C}_2\text{F}_4]$  by pressure measurements.
- (e) Laser photolysis with photofragment translational spectroscopy using TOF-MS to detect Br, Cl and  $\text{CF}_2$ . All  $\text{CClF}_2$  and  $\text{CBrF}_2$  radicals produced dissociate spontaneously to produce Cl or  $\text{Br} + \text{CF}_2$ .
- (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  $\text{CF}_2\text{Cl} + \text{Br}$  channel the branching ratio for  $\text{Br}(^2\text{P}_{1/2})$  and  $\text{Br}(^2\text{P}_{3/2})$  is determined to be  $0.41 \pm 0.05$ .

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## Preferred Values

### Absorption cross-sections of CF<sub>2</sub>CIBr at 295 K and 210 K.

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 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

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$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K
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

$\Phi = 1.0$  over the wavelength range 200–300 nm.

## Comments on Preferred Values

- 5 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
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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  $\sigma$  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  $\text{CF}_2$ , Cl, and Br at 193 nm and found that the  $\text{CF}_2\text{ClBr}$  was photodissociated to give  $\text{CF}_2$  with a quantum yield of unity, probably by initial production of  $\text{CF}_2\text{Cl}$  which was not collisionally stabilized under their conditions but went on to give  $\text{CF}_2 + \text{Cl}$ . 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  $\text{CF}_2\text{Cl}$  fragment, and a minor pathway involving initial rupture of the C-Cl bond was also detected. At 157.6 nm  $\text{CF}_2\text{ClBr}$  dissociates competitively in all three dissociation channels (2), (3 and (4), with 25% producing  $\text{CF}_2$  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).

$\text{CF}_2\text{ClBr}$  has been estimated to have a tropospheric lifetime against direct solar photoexcitation of 15 to 20 years (Burkholder et al., 1991; Molina et al., 1982).

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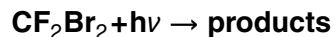
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### Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_2\text{Br}_2 + h\nu$	$\rightarrow \text{CF}_2\text{Br} + \text{Br}$ (1)	280 (est)	427
	$\rightarrow \text{CF}_2 + \text{Br} + \text{Br}$ (2)	419	286
	$\rightarrow \text{CF}_2 + \text{Br}_2$ (3)	226	529

### 5 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)

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## Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\Phi(\text{CF}_2\text{O})=1.14$ $\Phi(\text{Br}_2)=1.11$ $\Phi(-\text{CBr}_2\text{F}_2)=1.12$	206.2	Molina and Molina, 1983	(d)
$\Phi(\text{CF}_2)=1.03$ $\Phi(\text{Br}_2)=0.99$ $\Phi(-\text{CBr}_2\text{F}_2)=1.05$	247.7		
$\Phi(\text{CF}_2\text{O})=1.23$ $\Phi(\text{Br}_2)=1.28$	302.4		
$\Phi(\text{Br})=1.96\pm 0.25$ $\Phi(\text{Br})=1.63\pm 0.19$ $\Phi(\text{Br})=1.01\pm 0.15$	193 222 248	Talukdar et al., 1992	(e)
$\Phi(\text{CF}_2)=1.11\pm 0.22$ $\Phi(\text{CF}_2)=1.18\pm 0.30$	193 193	Talukdar et al., 1996	(e)
$\Phi(1)=0.84$ $\Phi(2)=0.15$ $\Phi(3)=\text{trace}$	234	Park et al., 2001	(f)
$\Phi(3)=0.04\pm 0.01$	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  $\text{CF}_2\text{Br}_2$  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

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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  $\text{CF}_2\text{Br}_2$ -air mixtures at 1 bar. The only photolysis products found were  $\text{CF}_2\text{O}$  and  $\text{Br}_2$ . The  $\text{CF}_2\text{O}$  and  $\text{CBr}_2\text{F}_2$  concentrations were monitored by FTIR, and the  $\text{Br}_2$  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  $\text{CF}_2\text{Br}_2$ -diluent (He,  $\text{N}_2$ , or Ar) mixtures was used with a small amount of  $\text{H}_2$  added to ensure rapid quenching of the  $\text{Br}(^2\text{P}_{1/2})$  produced to  $\text{Br}(^2\text{P}_{3/2})$ .  $\text{Br}(^2\text{P}_{3/2})$  was detected by resonance fluorescence and  $\text{CF}_2$  by UV absorption. The two values of  $\Phi(\text{CF}_2)$  cited were obtained by monitoring  $[\text{CF}_2]$  at 248.7 and 258.3 nm. The  $\text{Br}(^2\text{P}_{3/2})$  measurements were calibrated by  $\text{CH}_3\text{Br}$  photolysis at the same wavelength for which a quantum yield of unity was assumed. The  $\text{CF}_2$  measurements were calibrated using  $\text{C}_2\text{F}_4$  photolysis taking a quantum yield for  $\text{CF}_2$  production at 193 nm of 2.
- (f) Photodissociation dynamics of  $\text{CF}_2\text{Br}_2$  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  $\text{Br}_2$  in the  $\text{B}^3\Pi+\text{u}-\text{X}^1\Sigma+\text{g}$  transition.

## Preferred Values

### Absorption cross-sections of CF<sub>2</sub>Br<sub>2</sub> at 295 K and 210 K.

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 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

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$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 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

- 5 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
- 10 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

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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  $\sigma$  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  $\text{CF}_2\text{Br}_2$ -air mixtures at a pressure of 1 bar were  $\text{CF}_2\text{O}$  and  $\text{Br}_2$  and concluded that the quantum yield for photodissociation of  $\text{CBr}_2\text{F}_2$  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  $\text{CF}_2\text{Br}$ . Cameron et al. (2000) used LIF to detect vibrational distribution of nascent  $\text{CF}_2$  produced by photolysis of  $\text{CBr}_2\text{F}_2$  at discrete wavelengths in the range 223–260 nm. Their results showed that  $\text{CF}_2$  production at 246 nm was accompanied by the production of two Br fragments. However Hsu et al (2005) measured significant  $\text{Br}_2$  production ( $\phi=0.04$ ) at 248 nm using CRDS detection, and Park et al (2001) report seeing a  $\text{Br}_2$  elimination channel at 234 nm. Here is insufficient information to recommend  $\lambda$  dependence of  $\phi(\text{Br})$ , but it is recommended to use  $\phi(\text{Br})=1.0$  for tropospheric photolysis and  $\phi(\text{Br})=2.0$  for stratospheric photolysis.

Because its absorption extends into the 290–310 nm wavelength range,  $\text{CF}_2\text{Br}_2$  has a short tropospheric lifetime against direct solar photoexcitation, of about 3 years.

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$\text{CHBr}_3 + h\nu \rightarrow \text{products}$ 

## Primary photochemical processes

Reaction	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\lambda_{\text{threshold}} / \text{nm}$
$\text{CHBr}_3 + h\nu \rightarrow \text{CHBr}_2 + \text{Br}$ (1)	276	433
$\rightarrow \text{CHBr} + \text{Br}_2$ (2)	355	337

## 5 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
$\Phi(\text{Br})=0.74$ $\Phi(\text{Br}_2)=0.26$	234	Xu et al., 2002	(c)
$\Phi(\text{Br})=0.84$ $\Phi(\text{Br}_2)=0.16$	267		
$\Phi(\text{Br})=1.0$ $\Phi(\text{Br})=0.76 \pm 0.03$	302-306 266	Bayes et al., 2003	(d)
$\Phi(\text{Br}_2)=0.23 \pm 0.05$	248	Huang et al., 2004	(e)

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- (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  $\text{CHBr}_3$  studied using photofragment TOF-MS and velocity ion image imaging, following laser photolysis at 234 and 265 nm. Both excited spin orbit excited  $\text{Br}(^2\text{P}_{1/2})$  and ground  $\text{Br}(^2\text{P}_{3/2})$  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  $\lambda$  between 130–163 nm.
- (e) Laser photolysis at 248 nm with CRDS detection of nascent  $\text{Br}_2$  in the  $\text{B}^3\Pi+\text{u} - \text{X}^1\Sigma+\text{g}$  transition.

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## Preferred Values

### Absorption cross-sections of $\text{CHBr}_3$ at 296 K and 210 K.

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 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

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$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K
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			

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## Comments on Preferred Values

There have been two studies of the absorption cross-sections of  $\text{CHBr}_3$ . 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,  $\ln \sigma(\lambda, T) = (0.0618350 - 0.000241014 \lambda)(273 - T) - (2.37616 + 0.1475688 \lambda)$ , 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  $0.76 \pm 0.03$  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  $\text{Br}_2$  by TOF mass spectrometry from bromoform photolysis at 234 and 267 nm. Huang (2004) also observed  $\text{Br}_2$  production at 248 nm, using CRDS to probe the molecular fragment, and measured a quantum yield of  $0.23 \pm 0.05$ . On the other hand the experiments of McGovern et al. (2000) and Zou et al. (2004), using VUV ionisation photofragment transla-

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tional spectroscopy at 193 nm and at 248 nm respectively, suggest that Br<sub>2</sub> 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<sub>2</sub> are formed, any Br<sub>2</sub> will be rapidly photodissociated to 2Br in the sunlit atmosphere.

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### Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_2\text{BrCF}_2\text{Br} + h\nu \rightarrow \text{CF}_2\text{BrCF}_2 + \text{Br}$	280 (est)	427

### 5 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
$\Phi(\text{Br})=1.9\pm 0.1$	193	Zou et al., 2000	(d)
$\Phi(\text{Br})=1.9\pm 0.1$	233		
$\Phi(\text{Br})=1.4\pm 0.1$	266		

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## 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  $\text{CF}_2\text{BrCF}_2\text{Br}$ . Detection by VUV ionisation or REMPI.

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## Preferred Values

### Absorption cross-sections of CF<sub>2</sub>BrCF<sub>2</sub>Br at 296 K and 210 K.

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 295 K	$10^{20} \sigma/\text{cm}^2$ 210 K
190	108	119	240	13.4	11.5
192	114	124	242	10.7	8.95
194	119	128	244	8.47	6.89
196	123	131	246	6.69	5.25
198	125	133	248	5.23	2.95
200	125	133	250	4.05	2.93
202	125	132	252	3.09	2.15
204	121	129	254	2.36	1.56
206	117	125	256	1.77	1.13
208	112	119	258	1.32	0.807
210	105	112	260	0.978	0.576
212	98.6	104	262	0.724	0.391
214	94.5	96.1	264	0.535	0.275
216	83.4	85.0	266	0.394	0.191
218	75.6	79.0	268	0.290	0.134
220	67.8	70.3	270	0.212	0.093
222	60.2	62.0	272	0.155	
224	53.0	54.3	274	0.112	
226	46.2	46.8	276	0.082	
228	40.0	40.1	278	0.060	
230	34.2	33.9	280	0.044	
232	29.0	27.9			
234	24.3	22.6			
236	20.1	18.2			
238	16.5	14.5			

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## Quantum Yields

$\Phi(\text{Br})=2$  (in stratosphere).

$\Phi(\text{Br})=1$  (in troposphere).

### *Comments on Preferred Values*

5 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  
10 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 ( $\sim 200$  nm) Burkholder et al. (1991) report a 20% increase in the absorption cross-section in going from 295 K to 210 K, whereas  
15 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  $\sim 4\%$  lower than those of Burkholder et al. (1991) at short wavelengths but this difference increases in going to longer wavelengths, reaching  $\sim 40\%$  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).  
20

Photolysis is expected to occur with unit quantum efficiency by rupture of the C-Br bond to give  $\text{CF}_2\text{BrCF}_2 + \text{Br}$  and prompt dissociation of nascent  $\text{CF}_2\text{BrCF}_2$  to give a second Br atom is likely to predominate in stratospheric photolysis, which is the main atmospheric sink.  $\text{CF}_2\text{BrCF}_2\text{Br}$  has been estimated to have a tropospheric lifetime  
25 against direct solar photolysis of 34 years (Burkholder et al., 1991).

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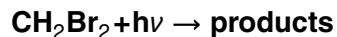
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### Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_2\text{Br}_2 + h\nu \rightarrow \text{CH}_2\text{Br} + \text{Br}$	292	410

### 5 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

- 10 (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.

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(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  $\text{CH}_2\text{Br}_2$  used covered the range  $0.05\text{--}47 \times 10^{-2}$  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  $\sim 0.6$  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  $\ln \sigma_T = \ln \sigma_{298\text{K}} + B(T - 298)$  and values of  $B$  were derived.

## Preferred Values

### Absorption cross-sections of $\text{CH}_2\text{Br}_2$ at 298 K and 210 K.

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 210 K	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$ 298 K	$10^{20} \sigma/\text{cm}^2$ 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			

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## Quantum Yields

$\Phi(\text{Br})=1$  for  $\lambda > 240$  nm.

### Comments on Preferred Values

5 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  $\sigma$  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).  
10 The results agree well in the region where they overlap and both find that  $\sigma$  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  
15 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  $\text{CH}_2\text{Br}_2$  undergoes a simple C-Br fission (Lee et al., 2003).

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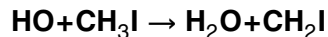
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## Appendix 4: IO<sub>x</sub> Reactions

### IV.A4.266



$$\Delta H^\circ = -63.1 \text{ kJ mol}^{-1}$$

5

#### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.1 \times 10^{-12} \exp[-(1119 \pm 205)/T]$	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(<sup>3</sup>P) atoms (from 193 nm pulsed laser photolysis of N<sub>2</sub>O in N<sub>2</sub>) in the presence of varying amounts of CH<sub>3</sub>I.

10

#### Preferred Values

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

$k = 4.3 \times 10^{-12} \exp(-1120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270–17030

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430 K.

### **Reliability**

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

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

### 5 **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-  
10 dependent study to date, is accepted and the pre-exponential factor is adjusted to fit the 298 K preferred value.

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15 E.: Atmos. Environ., 37, 1125, 2003.  
Gilles, M. K., Turnipseed, A. A., Talukdar, R. K., Rudich, Y., Villalta, P. W., Huey, L. G., Burkholder, J. B., and Ravishankara, A. R.: J. Phys. Chem., 100, 14005, 1996.

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HO+CF<sub>3</sub>I → products

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.2 \pm 0.2) \times 10^{-13}$	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		

5 **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<sub>3</sub>I 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<sub>3</sub>+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<sub>3</sub> in the presence of H<sub>2</sub>O to generate HO radicals. The cited rate coefficients and Arrhenius expression were obtained

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from experiments using 351 nm photolysis of HONO as the HO radical source. The CF<sub>3</sub>I concentrations were monitored by UV/visible absorption spectroscopy.

### Preferred Values

$k = 2.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

5  $k = 2.1 \times 10^{-11} \exp(-2000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270–370 K.

### Reliability

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

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

### 10 *Comments on Preferred Values*

Studies of this reaction have the potential for secondary reactions (including, in the pulsed photolysis systems, with CF<sub>3</sub>I 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  
15 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<sub>3</sub>I concentrations being monitored by UV/visible absorption spectroscopy.

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Berry, R. J., Yuan, J., Misra, A., and Marshall, P.: J. Phys. Chem. A, 102, 5182, 1998.

20 Brown, A. C., Canosa-Mas, C. E., and Wayne, R. P.: Atmos. Environ., 24A, 361, 1990.

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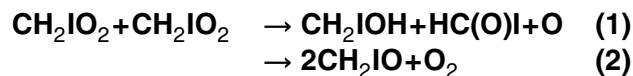
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#### IV.A4.268



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\sim 9 \times 10^{-11}$	295±2	Sehested et al., 1994	(a)

#### 5 Comments

(a) Pulse radiolysis UV absorption spectrometric study of  $\text{CH}_3\text{I}-\text{O}_2-\text{SF}_6$  mixtures at a total pressure of 1000 mbar.  $\text{CH}_2\text{IO}_2$  radicals were monitored by UV absorption with  $\sigma_{370} = (2.1 \pm 0.5) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . The interpretation of the kinetic data is complicated by the presence of  $\text{CH}_3\text{O}_2$  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

15 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

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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.

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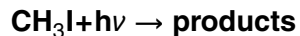
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### Primary photochemical processes

Reaction	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\lambda_{\text{threshold}} / \text{nm}$
$\text{CH}_3\text{I} + h\nu \rightarrow \text{CH}_3 + \text{I}({}^2\text{P}_{3/2})$ (1)	239	541
$\rightarrow \text{CH}_3 + \text{I}({}^2\text{P}_{1/2})$ (2)	330	362
$\rightarrow \text{CH}_2 + \text{HI}$ (3)	403	297

### 5 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)

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## 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  $\sigma=1.22\times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ , 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

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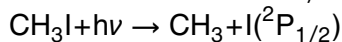
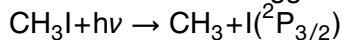
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from <230 nm to 365 nm with a maximum at 260 nm where the absorption cross section was  $\sigma = (1.09 \pm 0.08) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  at 298 K. The temperature dependence of the absorption cross section was determined over the range 243–333 K; broadening of the band was observed giving a significant decline in  $\sigma$  with decreasing temperature in the tropospheric photolysis region ( $\lambda > 290 \text{ nm}$ ).

(d) The absorption spectrum of  $\text{CH}_3\text{I}$  (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  $\sigma = 1.13 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  with a stated overall uncertainty of  $\pm 5\%$ . Significant temperature dependence of the absorption cross section was observed over the range 228–298 K, with a decrease in  $\sigma$  with decreasing temperature in the long wavelength tail. A second absorption band is indicated by an increase in  $\sigma$  below 210 nm.

(e) Photo-oxidation of  $\text{CH}_3\text{I}$ ; measurement of loss of  $\text{CH}_3\text{I}$  and yield of  $\text{I}_2$  product.  $\Phi(-\text{CH}_3\text{I}) = 1.0$ ;  $\Phi(\text{I}_2) = 0.5$ .

(f) Translational energy of the I atoms produced in 266 nm photolysis of  $\text{CH}_3\text{I}$  in a molecular beam. Suggested the following primary processes:



with  $\text{I}(^2\text{P}_{3/2})$  production at 78% of the primary process.

(g) Pulsed tunable laser photolysis of  $\text{CH}_3\text{I}$ , with  $\text{I}(^2\text{P}_{1/2})$  detection by infra-red fluorescence at  $1.315 \mu\text{m}$ .  $\Phi\{\text{I}(^2\text{P}_{1/2})\}$  increased from 0.05 to 0.81 over the wavelength range 308–248 nm.

(h) Branching ratio for  $\text{I}(^2\text{P}_{1/2})/\text{I}(^2\text{P}_{3/2})$  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).

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## Preferred Values

### Absorption cross-sections of CH<sub>3</sub>I at 298 K

Wavelength/nm	10 <sup>20</sup> $\sigma$ /cm <sup>2</sup>	10 <sup>3</sup> B/K <sup>-1</sup>
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

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Wavelength/nm	$10^{20} \sigma/\text{cm}^2$	$10^3 B/\text{K}^{-1}$
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:  $\ln \sigma = \ln \sigma(298) + B(T - 298/\text{K})$

## Quantum Yield

$\Phi_1 + \Phi_2 = 1.0$  over the wavelength range 210–360 nm.

## 5 *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  $\sim$  210 nm and is attributed to a  $\sigma \rightarrow n$  transition. The recently 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

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measurements at  $\lambda > 300$  nm, but are significantly higher by  $\sim 20\%$  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  $\sigma$  at the band head and a decrease in  $\sigma$  in the long wavelength tail of absorption. The temperature dependence of  $\text{CH}_3\text{I}$  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:  $\ln \sigma = \ln \sigma(298) + B(T - 298/K)$  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:  $\text{I}({}^2\text{P}_{1/2}) \rightarrow \text{I}({}^2\text{P}_{3/2}) + h\nu$  observed at  $1.315 \mu\text{m}$  in the near-UV flash photolysis of  $\text{CH}_3\text{I}$  (Kasper and Pimentel, 1964). State-selected photofragment spectroscopy has shown that I atoms are produced in both the ground  $\text{I}({}^2\text{P}_{3/2})$  and the electronically excited  $\text{I}({}^2\text{P}_{1/2})$  state. The relative yields of  $\text{I}({}^2\text{P}_{1/2})$  increases with decreasing wavelength below 304 nm to a maximum near the maximum in the

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A-band absorption of CH<sub>3</sub>I near 260 nm. This can be rationalised in terms of the correlations of I(<sup>2</sup>P<sub>1/2</sub>) and I(<sup>2</sup>P<sub>3/2</sub>) states with the <sup>3</sup>Q<sub>o+</sub>, <sup>1</sup>Q<sub>1</sub> and <sup>3</sup>Q<sub>1</sub> electronic states, which have λ<sub>max</sub> at 261 nm, 240 nm and 300 nm respectively (Gedanken et al., 1975).

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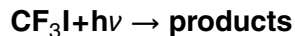
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### Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_3\text{I} + h\nu \rightarrow \text{CF}_3 + \text{I}({}^2\text{P}_{3/2})$ (1)	230	521
$\rightarrow \text{CF}_3 + \text{I}({}^2\text{P}_{1/2})$ (2)	320	374

### 5 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
$\Phi\{\text{I}({}^2\text{P}_{1/2}); \text{I}({}^2\text{P}_{3/2})\}$	266	Riley and Wilson, 1972	(d)
$\Phi\{\text{I}({}^2\text{P}_{1/2}); \text{I}({}^2\text{P}_{3/2})\}$	304	Kang et al., 1996	(e)
$\Phi\{\text{I}({}^2\text{P}_{1/2}); \text{I}({}^2\text{P}_{3/2})\}$	275-303	Furlan et al., 1996	(f)

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## Comments

- (a) Absorption coefficients for purified  $\text{CF}_3\text{I}$  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  $\sigma=6.0\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ .
- (b) The absorption spectrum of  $\text{CF}_3\text{I}$  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  $\sigma=6.8\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ . 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  $\text{CF}_3\text{I}$  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  $\sigma=(6.0\pm 0.1)\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ . A second band extends into the vacuum UV. The temperature dependence was determined for 243–333 K.
- (d) Translational energy of the I atoms produced in 266 nm photolysis of  $\text{CF}_3\text{I}$  in a molecular beam. Suggested the following primary processes:  
 $\text{CF}_3\text{I}+h\nu\rightarrow\text{CF}_3+\text{I}(^2\text{P}_{3/2})$   
 $\text{CF}_3\text{I}+h\nu\rightarrow\text{CF}_3+\text{I}(^2\text{P}_{1/2})$   
with  $\text{I}(^2\text{P}_{3/2})$  production at 78% of the primary process.
- (e) Relative yield of  $\text{I}(^2\text{P}_{1/2})/\text{I}(^2\text{P}_{3/2})$  determined by (2+1) REMPI and pulsed field TOF-MS following laser photodissociation of  $\text{CF}_3\text{I}$ .  $\Phi\{\text{I}(^2\text{P}_{1/2})\}=0.69$ .
- (f) Relative yield of  $\text{I}(^2\text{P}_{1/2})/\text{I}(^2\text{P}_{3/2})$  obtained by high resolution photofragment trans-

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lational 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.

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## Preferred Values

### Absorption cross-sections of CF<sub>3</sub>I at 298 K

Wavelength/nm	10 <sup>20</sup> σ/cm <sup>2</sup>	10 <sup>3</sup> B/K <sup>-1</sup>
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

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Wavelength/nm	$10^{20} \sigma/\text{cm}^2$	$10^3 B/\text{K}^{-1}$
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:  $\ln \sigma = \ln \sigma(298) + B(T - 298)/K$

## Quantum Yield

$\Phi_1 + \Phi_2 = 1.0$  over the wavelength range 210–360 nm.

## 5 *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  $\sigma$  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  $\text{CF}_3 + \text{I}$ . State-selected photofragment spectroscopy has shown that I atoms are produced predominantly in the excited state  $\text{I}(^2\text{P}_{1/2})$ , following photodissociation

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of CF<sub>3</sub>I near the band maximum. The branching ratio for: I(<sup>2</sup>P<sub>1/2</sub>)/I(<sup>2</sup>P<sub>3/2</sub>) 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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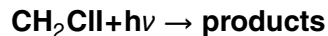
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### Primary photochemical processes

Reaction	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\lambda_{\text{threshold}} / \text{nm}$
$\text{CH}_2\text{ClI} + h\nu \rightarrow \text{CH}_2\text{Cl} + \text{I}$ (1)	217	551
$\rightarrow \text{CH}_2\text{I} + \text{Cl}$ (2)	344	347

### 5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
235–390	Rattigan et al., 1997	(a)
200–380	Roehl et al., 1997	(b)

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## 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<sub>2</sub>ClI (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  $\sigma=(1.21\pm0.07)\times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> 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  $\sigma$  with decreasing temperature in the tropospheric photolysis region ( $\lambda > 290$  nm).

(b) The absorption spectrum of CH<sub>2</sub>ClI (purity 97%) was recorded by diode array spectrometry with a resolution of 0.3 nm. The absolute cross section at the max-

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imum of absorption at 270 nm was  $\sigma = 1.35 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  with a stated overall uncertainty of  $\pm 5\%$ . Significance temperature dependence of the absorption cross section was observed over the range 228–298 K, with a decrease in  $\sigma$  with a decrease in temperature in the long wavelength tail. A second absorption band is indicated by an increase in  $\sigma$  below 220 nm.

- (c) Laser photolysis of  $\text{CH}_2\text{ClI}$ ; measurement of yield of  $\text{I}_2$  by time resolved laser absorption spectroscopy at 514.5 nm.
- (d) Laser Photolysis-REMPI detection of  $\text{I}({}^2\text{P}_{1/2})$  and  $\text{I}({}^2\text{P}_{3/2})$ .
- (e) Laser Photolysis-REMPI detection of  $\text{Cl}({}^2\text{P}_{1/2})$  and  $\text{Cl}({}^2\text{P}_{3/2})$ .  $\Phi$  determined relative to  $\Phi\{\text{I}({}^2\text{P}_{1/2})\}$  production at the same wavelength.

## Preferred Values

### Absorption cross-sections of CH<sub>2</sub>ClI at 298 K

Wavelength/nm	10 <sup>20</sup> $\sigma$ /cm <sup>2</sup>	10 <sup>3</sup> $B/K^{-1}$
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

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Wavelength/nm	$10^{20} \sigma/\text{cm}^2$	$10^3 B/\text{K}^{-1}$
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:  $\ln \sigma = \ln \sigma(298) + B(T - 298/K)$   
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## Quantum Yield

$\Phi_1 + \Phi_2 = 1.0$  over the wavelength range 230–390 nm; no recommendation for  $\Phi_2/\Phi_1$

### Comments on Preferred Values

5 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 ( $1.5 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ ). The preferred values for the cross-sections are a simple  
10 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  $\text{CH}_2\text{CI}$  studied by Schmitt and Comes (1987) indicated dissociation via reaction (1), in line with other alkyl iodides, occurring with a quantum  
15 yield of unity. The quantum yield of  $\text{I}(^2\text{P}_{1/2})$  are reported by Senapati et al. (2002), who observed a similar trend with wavelength as that observed for photolysis of  $\text{CH}_3\text{I}$ . This suggests that the photodissociation occurs from 3 upper states similar to methyl iodide. However, Senapati and Das 2004 observed  $\text{Cl}(^2\text{P}_{1/2})$  production and measured yields (relative to  $\text{I}(^2\text{P}_{1/2})$ ), which decrease with increasing wavelength in the range  $222 \leq \lambda \leq 304 \text{ nm}$ . An inter-chromophore energy transfer mechanism between C-I and C-Cl  
20 chromophore is proposed to rationalise  $\text{Cl}(^2\text{P}_{1/2})$  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<sub>2</sub>Brl+hν → products****Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH <sub>2</sub> Brl+hν → CH <sub>2</sub> Br+I (1)	214	559
→ CH <sub>2</sub> I+Br (2)	280	427
→ CH <sub>2</sub> +IBr (3)	369	324

5 **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**

- 10 (a) Absorption coefficients for CH<sub>2</sub>Brl (purity 98%) were determined by diode array spectrometry with a spectral resolution of 0.6 nm. The purity of the CH<sub>2</sub>Brl  
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sample was 92%, the main impurities being  $\text{CH}_2\text{Br}_2$  (6.5%) and  $\text{CH}_2\text{I}_2$  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  $\text{CH}_2\text{BrI}$  were observed with maxima at 215 nm and 270 nm where the absorption cross sections were  $\sigma = (5.67 \pm 0.34) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  and  $\sigma = (2.34 \pm 0.14) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  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  $\sigma$  with decreasing temperature in the tropospheric photolysis region ( $\lambda > 290 \text{ nm}$ ).

- (2) Photodissociation of  $\text{CH}_2\text{BrI}$  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.
- (3) Product state distributions measured for laser photodissociation  $\text{CH}_2\text{BrI}$  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  $^2\text{P}_{3/2}$  and excited state  $^2\text{P}_{1/2}$  atoms in ratio of 1.0:0.75. At shorter wavelengths elimination of IBr was also observed.

## Preferred Values

### Absorption cross-sections of CH<sub>2</sub>Brl at 298 K

Wavelength/nm	10 <sup>20</sup> $\sigma$ /cm <sup>2</sup>	10 <sup>3</sup> B/K <sup>-1</sup>
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

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Wavelength/nm	$10^{20} \sigma/\text{cm}^2$	$10^3 B/\text{K}^{-1}$
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:  $\ln \sigma = \ln \sigma(298) + B(T - 298)/K$

## Quantum Yield

$\Phi_1 = 1.0$  over the wavelength range 290–380 nm.

5

## 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

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group agree well with other literature data and the CH<sub>2</sub>Brl data can be considered reliable. The absorption spectrum agrees with earlier reported spectra (Lee and 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<sub>2</sub>Brl 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<sub>2</sub>I<sub>2</sub>+hν → products****Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH <sub>2</sub> I <sub>2</sub> +hν → CH <sub>2</sub> I+I (1)	219	547
→ CH <sub>2</sub> +I <sub>2</sub> (2)	335	357

5 **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
$\Phi(\text{I}_2)$	300	Schmitt and Comes, 1980	(e)
$\Phi\{\text{I}(\text{}^2\text{P}_{1/2}; \text{I}(\text{}^2\text{P}_{3/2})\}$	254	Baughcum and Leone, 1980	(f)
$\Phi\{\text{I}(\text{}^2\text{P}_{1/2})\}$	248–340	Koffend and Leone, 1981	(g)

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- (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  $\sigma=4.07 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .
- (b) The absorption spectrum of  $\text{CH}_2\text{I}_2$  was recorded by conventional UV absorption spectrometry. The absolute cross-section at the first maximum of absorption at 286 nm was  $\sigma=3.92 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .
- (c) The absorption spectrum of  $\text{CH}_2\text{I}_2$  (purity 97%) was recorded by diode array spectrometry with a resolution of 0.3 nm. The third absorption maximum occurred at 210 nm. The absolute cross-section at the first maximum of absorption at 290 nm was  $\sigma=3.84 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  with a stated overall uncertainty of  $\pm 5\%$ . 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  $\sigma$  with decreasing temperature in the long wavelength tail.
- (d) Absorption coefficients for  $\text{CH}_2\text{I}_2$  (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  $\sigma=(1.62 \pm 0.10) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  and  $\sigma=(3.78 \pm 0.23) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ , 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  $\sigma$  with decreasing temperature in the tropospheric photolysis region ( $\lambda > 290 \text{ nm}$ ).
- (e) Pulsed laser photolysis of  $\text{CH}_2\text{I}_2$ ; measurement of yield of  $\text{I}_2$  by absorption spectrometry. Primary products deduced to be I atoms, partially in the excited state.

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(f) Pulsed tunable laser photolysis of  $\text{CH}_2\text{I}_2$ , with  $\text{I}({}^2\text{P}_{1/2})$  and excited  $\text{CH}_2\text{I}_2$  detection by infra red emission.

(g) Pulsed tunable laser photolysis of  $\text{CH}_2\text{I}_2$ , with  $\text{I}({}^2\text{P}_{1/2})$  detection by infra red fluorescence at  $1.315 \mu\text{m}$ .  $\Phi\{\text{I}({}^2\text{P}_{1/2})\}$  increased from zero to 0.46 over the wavelength range 340 – 248 nm.

## Preferred Values

### Absorption cross-sections of $\text{CH}_2\text{I}_2$ at 298 K

Wavelength/nm	$10^{20} \sigma/\text{cm}^2$	$10^3 B/\text{K}^{-1}$
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

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Wavelength/nm	$10^{20} \sigma/\text{cm}^2$	$10^3 B/\text{K}^{-1}$
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	.77
370	3.4	8.25
375	1.93	11.3
380	1.16	
385	0.77	

Temperature dependence given by:  $\ln \sigma = \ln \sigma(298) + B(T - 298/K)$

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## 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<sub>2</sub>I<sub>2</sub>. 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  $\ln \sigma = \ln \sigma(298) + B(T - 298/K)$ . 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<sub>2</sub>I<sub>2</sub> 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  $\lambda=215$  nm. A significant fraction of I atoms are formed in the excited state in the tropospheric photolysis of CH<sub>2</sub>I<sub>2</sub>.

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