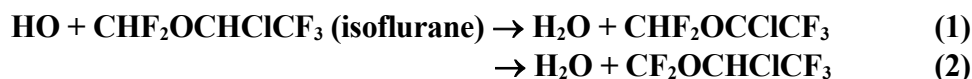


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oClOx71; IV.2.145

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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		
$(1.45 \pm 0.16) \times 10^{-14}$	296	Sulbaek Andersen et al. (2012)	PLP/LIF (a)
<i>Relative Rate Coefficients</i>			
$<3 \times 10^{-13}$	300 ± 3	McLoughlin et al., 1993	RR (b)
<i>Branching Ratios</i>			
$k_1/k = 0.95 \pm 0.03$	295	Wallington et al., 2002	(c)
$k_2/k = 0.05 \pm 0.03$			

Comments

- (a) HO radicals were generated by the 248 nm photolysis of ozone in the presence of CH₄. Photolysis of O₃ gives O(¹D) atoms which react with CH₄ to give HO radicals. The decay of HO radicals was measured using LIF at 308 nm in the presence of CHF₂OCHClCF₃.
- (b) HO radicals were generated by the photolysis of CH₃ONO-NO-CHF₂OCHClCF₃-diethyl ether air mixtures at ~1 bar pressure. The concentrations of CHF₂OCHClCF₃ 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 using $k(\text{HO} + \text{diethyl ether}) = 1.22 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K (Calvert et al, 2011).
- (c) HO radicals were generated by the photolysis of CH₃ONO-NO-CHF₂OCHClCF₃-C₂H₄ air mixtures at 933 mbar total pressure. The formation of CHF₂OC(O)CF₃ and COF₂ and the loss of C₂H₄ were measured by FTIR spectroscopy. The loss of CHF₂OCHClCF₃ was calculated from the observed loss of C₂H₄. Wallington et al. (2002) assumed a rate coefficient ratio of $k(\text{HO} + \text{C}_2\text{H}_4)/k(\text{HO} + \text{CHF}_2\text{OCHClCF}_3) = 450$ to calculate the loss of CHF₂OCHClCF₃ and reported the formation of CHF₂OC(O)CF₃ and COF₂ in molar yields of $85 \pm 10\%$ and $5 \pm 1\%$, respectively. Rescaling to $k(\text{HO} + \text{C}_2\text{H}_4)/k(\text{HO} + \text{CHF}_2\text{OCHClCF}_3) = 7.9 \times 10^{-12}/1.5 \times 10^{-14} = 527$ (Atkinson et al., 2006) gives molar yields of CHF₂OC(O)CF₃ and COF₂ of $100 \pm 12\%$ and $6 \pm 2\%$, respectively. Assuming that reaction (1) leads to the formation of CHF₂OC(O)CF₃ while reaction (2) leads to the formation of COF₂ in a yield of 100 or 200% (Wallington et al.,

2002) gives $k_2/k = 0.05 \pm 0.03$. Assuming that $k_1/k + k_2/k = 1$, then $k_1/k = 0.95 \pm 0.03$.

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.5×10^{-14}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.1 \times 10^{-12} \exp(-1280/T)$	250-430
$k_1/(k_1+k_2)$	0.95	298
$k_2/(k_1+k_2)$	0.05	298
<i>Reliability</i>		
$\Delta \log k$	0.10	298
$\Delta(E/R)$	± 250	250-430
$\Delta k_1/(k_1+k_2)$	0.03	298
$\Delta k_2/(k_1+k_2)$	0.03	298

Comments on Preferred Values

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 $\text{CHF}_2\text{OCF}_2\text{CHFCl}$ 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 rate coefficient measured at 296 K by Sulbaek Andersen et al. (2012) is in good agreement with the results from Tokuhashi 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. The preferred branching ratios $k_1/(k_1+k_2)$ and $k_2/(k_1+k_2)$ are derived from the measurements by Wallington et al. (2002) of the yields of $\text{CF}_3\text{C}(\text{O})\text{OCHF}_2$ and COF_2 from the OH radical initiated oxidation of $\text{CF}_3\text{CHClOCHF}_2$ in 700 Torr of air at 295 K in the presence of NO.

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