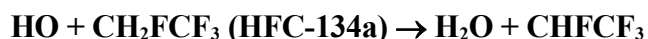


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx19

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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
$1.1 \times 10^{-12} \exp[-(1424 \pm 35)/T]$	249-473	Jeong et al., 1984	DF-RF
$(8.44 \pm 0.73) \times 10^{-15}$	298		
$5.8 \times 10^{-12} \exp[-1350/T]$	231-423	Brown et al., 1990	DF-RF
6.25×10^{-15}	298		
$3.7 \times 10^{-12} \exp[-(1990 \pm 280)/T]$	270-400	Liu et al., 1990	FP-RF
$(5.18 \pm 0.70) \times 10^{-15}$	298		
$5.7 \times 10^{-13} \exp[-(1430 \pm 60)/T]$	223-324	Gierczak et al., 1991	DF-LMR/FP-LIF (a)
$(4.34 \pm 0.35) \times 10^{-15}$	298		
$(2.38 \pm 0.22) \times 10^{-15}$	270	Zhang et al., 1992	DF-RF
$1.03 \times 10^{-12} \exp[-(1588 \pm 52)/T]$	298-460	Orkin and Khamaganov, 1993	DF-EPR
$(5.00 \pm 0.44) \times 10^{-15}$	298		
$9.9 \times 10^{-13} \exp[-(1640 \pm 150)/T]$	255-424	Leu and Lee, 1994	DF-RF
$(3.9 \pm 0.6) \times 10^{-15}$	298		
$(4.6 \pm 0.5) \times 10^{-15}$	295	Bednarek et al., 1996	LP-UVA
<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)
3.76×10^{-15}	298		
$1.84 \times 10^{-18} T^2 \exp[-(1129 \pm 44)/T]$	298-358	DeMore, 1993	RR (b,d)
3.70×10^{-15}	298		
$1.93 \times 10^{-18} T^2 \exp[-(1132 \pm 79)/T]$	298-358	DeMore, 1993	RR (b,e)
3.84×10^{-15}	298		
$(3.90 \pm 0.48) \times 10^{-15}$	298 ± 2	Barry et al., 1995	RR (f)
$(4.19 \pm 0.19) \times 10^{-15}$	298 ± 2	Barry et al., 1995	RR (g)

Comments

- (a) Measurements were performed up to a temperature of 450 K. The Arrhenius expression only covers the temperature range 223-324 K to avoid curvature in the Arrhenius plot.
- (b) Relative rate method. HO radicals were generated by the photolysis of $\text{O}_3\text{-H}_2\text{O-O}_2\text{-Ar}$ mixtures at 254 nm. The CH_2FCF_3 , CH_4 , CH_3CCl_3 , and CHF_2CF_3 concentrations were monitored during the experiments by FTIR absorption spectroscopy. The measured rate coefficient ratios of

$k(\text{HO} + \text{CH}_4)/k(\text{HO} + \text{CH}_2\text{FCF}_3) = (2.24 \pm 0.78) \exp[-(82 \pm 115)/T]$, $k(\text{HO} + \text{CH}_3\text{CCl}_3)/k(\text{HO} + \text{CH}_2\text{FCF}_3) = (1.22 \pm 0.17) \exp[(219 \pm 44)/T]$ 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 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), $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation) 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 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 CH_2FCF_3 and CH_3CCl_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 K (IUPAC, current recommendation).
 (g) Relative rate method. HO radicals were generated by the photolysis of O_3 in the presence of water vapor. Irradiations of $\text{O}_3\text{-H}_2\text{O-CH}_2\text{FCF}_3\text{-CH}_2\text{FCHF}_2\text{-air}$ mixtures were carried out at $298 \pm 2 \text{ K}$ and the concentrations of CH_2FCF_3 and CH_2FCHF_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 $k(\text{HO} + \text{CH}_2\text{FCHF}_2) = 1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).

Preferred Values

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

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

Comments on Preferred Values

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

The absolute rate coefficients of Martin and Paraskevopoulos (1983), Liu et al. (1990), Gierczak et al. (1991), Zhang et al. (1992), Orkin and Khamaganov (1993), Leu and Lee (1994), Bednarek et al. (1996), and the relative rate coefficients of Barry et al. (1995) have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, giving $k = 1.0 \times 10^{-18} T^2 \exp(-885/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range $220\text{-}460 \text{ K}$. 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 $B = D$

+ 2*T*. This expression yields rate coefficients that are 10-15% higher than those calculated from the rate coefficient expressions tabulated for DeMore (1993).

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