

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx20

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$$\Delta H^\circ = -58.4 \text{ kJ mol}^{-1}$$

Rate coefficient data

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

Comments

- HO radicals were generated by the photolysis of O₃-H₂O-O₂-Ar mixtures at 254 nm. The concentrations of CHF₂CHF₂ and CH₃CCl₃ 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 $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- HO radicals were generated by the photolysis of O₃-H₂O-O₂-Ar mixtures at 254 nm. The concentrations of CHF₂CHF₂ and CH₂FCF₃ 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).
- HO radicals were generated by photolysis of O₃-H₂O-O₂-Ar mixtures at 254 nm. The concentrations of CHF₂CHF₂ and CHF₂CF₃ 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.

$\Delta(E/R) = \pm 300$ 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 $A = C e^2 T^2$ and $B = D + 2T$.

References

Clyne, M. A. A. and Holt, P. M.: J. Chem. Soc. Faraday Trans. 2, 75, 582, 1979.

DeMore, W. B.: Geophys. Res. Lett. 20, 1359, 1993.

IUPAC: <http://iupac.pole-ether.fr>, 2013.