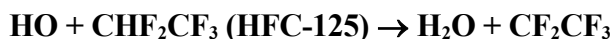


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx21

Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

The citation for this data sheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Wallington, T. J.: Atmos. Chem. Phys., 9, 4141, 2008; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

This datasheet last evaluated: June 2015; last change in preferred values: June 2011



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

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)
$(1.82 \pm 0.23) \times 10^{-15}$	296	Young et al., 2009	RR (b)

Comments

- (a) HO radicals were generated by the photolysis of O₃ in the presence of water vapor at 254 nm. Irradiations of O₃-H₂O-CHF₂CF₃-CH₄-O₂-N₂ (or Ar) mixtures were carried out, and the concentrations of CHF₂CF₃ and the CH₄ were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio $k(\text{HO} + \text{CH}_4)/k(\text{HO} + \text{CF}_3\text{CHF}_2) = 3.9 \pm 0.50$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_4) = 6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson et al., 2006).
- (b) HO radicals were generated by the photolysis of CH₃ONO in CHF₂CF₃-C₂H₄-CH₃ONO-NO mixtures in 933 mbar of N₂/O₂ diluent. The loss of CHF₂CF₃ was monitored indirectly by observing the formation of its oxidation product COF₂ and assuming a 200% molar yield (Wallington et al., 1994). COF₂ and C₂H₄ were measured by FTIR spectroscopy. The measured rate coefficient ratio $k(\text{HO} + \text{CHF}_2\text{CF}_3)/k(\text{HO} + \text{C}_2\text{H}_4) = (2.30 \pm 0.29) \times 10^{-4}$ was placed on an absolute basis using $k(\text{HO} + \text{C}_2\text{H}_4) = 7.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006).

Preferred Values

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

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

Reliability

$$\Delta \log k = \pm 0.12 \text{ at } 298 \text{ K.}$$

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

Comments on Preferred Values

The relatively high results of Clyne and Holt (1979) and Brown et al. (1990) suggest the presence of reactive impurities in the CHF₂CF₃ samples used in their studies. These data were therefore not used in the evaluation. At 298 K, the rate coefficients of DeMore (1992), Talukdar et al. (1991), and Young et al. (2009) agree to within 10%; the rate coefficient of Martin and Paraskevopoulos (1983) is 30% higher than the corresponding value of Talukdar et al. (1991). The rate coefficient data of Martin and Paraskevopoulos (1983), Talukdar et al. (1991), and DeMore (1992) were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 9.24 \times 10^{-19} T^2 \exp(-1120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 $A = C e^2 T^2$ and $B = D + 2T$.

References

- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006
- Brown, A. C., Canosa-Mas, C. E., Parr, A. D. and Wayne, R. P., Atmos. Environ. 24A, 2499, 1990.
- Clyne, M. A. A. and Holt, P. M.: J. Chem. Soc. Faraday Trans. 2, 75, 582, 1979.
- DeMore, W. B.: Optical Methods in Atmospheric Chemistry, Soc. Photo-Optic Instrum. Eng. 1715, 72, 1992.
- Martin, J.-P. and Paraskevopoulos, G.: Can. J. Chem. 61, 861, 1983.
- Talukdar, R., Mellouki, A., Gierczak, T., Burkholder, J. B., McKeen, S. A. and Ravishankara, A. R.: J. Phys. Chem. 95, 5815, 1991.
- Wallington, T. J., Schneider, W. F., Worsnop, D. R., Nielsen, O. J., Sehested, J., DeBruyn, W. , and Shorter, J. A.: Environ. Sci. Tech., 28, 320A, 1994.
- Young C. J., Hurley, M. D. Wallington, T. J., and Mabury, S. A.: Chem. Phys. Lett., 473, 251, 2009.

