

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx12

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: March 2005.



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

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)
1.71×10^{-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		
<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)
2.42×10^{-16}	298		
$6.19 \times 10^{-19} T^2 \exp[-(1523 \pm 34)/T]$	253-343	Chen et al., 2003	RR (d,e)
3.32×10^{-16}	298		
$1.12 \times 10^{-18} T^2 \exp[-(1706 \pm 44)/T]$	253-343	Chen et al., 2003	RR (d,f)
3.25×10^{-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 H₂O at 185 nm or of O₃-H₂O mixtures in the UV in H₂O (or H₂O-O₃)-CHF₃-CHF₂CF₃-N₂-O₂ mixtures. The concentrations of CHF₃ and CHF₂CF₃ 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 H₂O at 254 nm in the presence of a continuous flow of a 3% O₃ in O₂ mixture. The concentrations of CHF₃ and reference compounds were measured by GC-FID. 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 CHF_2CF_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 CHF_2Cl . 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.

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

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 $A = C e^2 T^2$ and $B = D + 2T$. The relative rate data of Hsu and DeMore (1995) are ~10% lower than the preferred values.-

References

- Bera, R. K. and Hanrahan, R. J.: *Radiat. Phys. Chem.* 32, 579, 1988.
Chen, L., Kutsuna, S., Tokuhashi, K. and Sekiya, A.: *Int. J. Chem. Kinet.* 35, 317, 2003.
Clyne, M. A. A. and Holt, P. M.: *J. Chem. Soc. Faraday Trans. 2*, 75, 582, 1979.
Howard C. J. and Evenson, K. M.: *J. Chem. Phys.* 64, 197, 1976.
Hsu, K.-J. and DeMore, W. B.: *J. Phys. Chem.* 99, 1235, 1995.
IUPAC: <http://iupac.pole-ether.fr>, 2013.
Jeong, K.-M. and Kaufman, F.: *J. Phys. Chem.* 86, 1808, 1982.
Jeong, K.-M., Hsu, K.-J., Jeffries, J. B. and Kaufman, F.: *J. Phys. Chem.* 88, 1222, 1984.
Medhurst, L. J., Fleming, J. and Nelson, H. H.: *Chem. Phys. Lett.* 266, 607, 1997.
Nip, W. S., Singleton, D. L., Overend, R. and Paraskevopoulos, G.: *J. Phys. Chem.* 83, 2440, 1979.
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.

