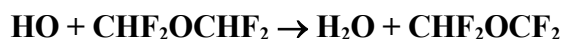


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx27

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 29th March 2005.



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.47 \pm 0.2) \times 10^{-14}$	296	Zhang et al., 1992	FP-RF
$5.4 \times 10^{-13} \exp[-(1560 \pm 200)/T]$	269-312	Garland et al., 1993	LP-LIF
$(3.0 \pm 0.7) \times 10^{-15}$	295		
$6.3 \times 10^{-13} \exp[-(1646 \pm 76)/T]$	277-370	Orkin et al., 1999	FP-RF
$(2.52 \pm 0.17) \times 10^{-15}$	298		
<i>Relative Rate Coefficients</i>			
$2.36 \times 10^{-18} T^2 \exp[-(1366 \pm 62)/T]$	298-368	Hsu and DeMore, 1995	RR (a)
2.1×10^{-15}	298		
$2.12 \times 10^{-18} T^2 \exp[-(1313 \pm 100)/T]$	273-464	Wilson et al., 2001	RR (b)
2.29×10^{-15}	298		

Comments

- (a) HO radicals were generated from the photolysis of H₂O at 185 nm or of O₃-H₂O mixtures in the UV (254 nm) in H₂O. The concentrations of CHF₂OCHF₂ and CH₃CCl₃ were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CHF}_2\text{OCHF}_2)/k(\text{HO} + \text{CH}_3\text{CCl}_3) = (1.05 \pm 0.20) \exp[-(456 \pm 62)/T]$ is placed on an absolute basis by using the rate coefficient for $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- (b) HO radicals were generated from the photolysis of H₂O vapour in the reaction mixture at 185 nm. The concentrations of CHF₂OCHF₂ and CF₃CHF₂ were monitored by GCMS. An Arrhenius plot of the Wilson et al. (2001) data gives a rate coefficient ratio of $k(\text{HO} + \text{CHF}_2\text{OCHF}_2)/k(\text{HO} + \text{CF}_3\text{CHF}_2) = (2.29 \pm 0.06) \exp[-(193 \pm 10)/T]$ over the temperature range 273-465 K. The rate coefficient ratio was 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).

Preferred Values

$k = 2.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.9 \times 10^{-12} \exp(-2020/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270 - 460 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

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

Comments on Preferred Values

The absolute rate coefficients of Orkin et al. (1999) and the relative rate coefficients of Hsu and DeMore (1995) and Wilson et al. (2001) are in good agreement over the temperature range 273-

370 K. The 296 K rate coefficient of Zhang et al. (1992) is an order of magnitude higher than all other values, presumably due to the presence of impurities in their CHF₂OCHF₂ samples. The measurements of Garland et al. (1993) are scattered. Thus, neither the data of Zhang et al. (1992) nor the data of Garland et al. (1993) were used in the evaluation.

The preferred values were obtained from the rate coefficient data of Hsu and DeMore (1995), Orkin et al. (1999) and Wilson et al. (2001). These rate coefficient data were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 2.22 \times 10^{-18} T^2 \exp(-1338/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 273-464 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 340 K with $A = C e^2 T^2$ and $B = D + 2T$.

Good et al. (1999) have performed experiments and ab initio calculations to determine the mechanism of CHF₂OCHF₂ oxidation under atmospheric conditions (no kinetic data were reported). Activation barriers were calculated for various steps, and an oxidation mechanism was described.

References

- Garland, N. L., Medhurst, L. J. and Nelson, H. H.: J. Geophys. Res. 98, 23107, 1993.
Good, D. A., Kamboures, M., Santiano, R. and Francisco, J. S.: J. Phys. Chem. A. 103, 9230, 1999.
Hsu, K.-J. and DeMore, W. B.: J. Phys. Chem. 99, 11141, 1995.
IUPAC: <http://iupac.pole-ether.fr>, 2013.
Orkin, V. L., Villenave, E., Huie, R. E. and Kurylo, M. J.: J. Phys. Chem. A. 103, 9770, 1999.
Wilson, E. W., Jr., Sawyer, A. A. and Sawyer, H. A., J. Phys. Chem. A. 105, 1445, 2001.
Zhang, Z., Saini, R. D., Kurylo, M. J. and Huie, R. E., J. Phys. Chem. 96, 9301, 1992.