

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx34

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This data sheet updated: 29th March 2005.



Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.8 \times 10^{-13} \exp[(910 \pm 220)/T]$	210-363	Maricq et al., 1994	FP-UVA (a)
$(4.7 \pm 1.7) \times 10^{-12}$	295		
$(4.0 \pm 2.0) \times 10^{-12}$	296	Hayman and Battin-Leclerc, 1995	LP-UVA (b)
$(3.3 \pm 1.5) \times 10^{-12}$	323		
$(2.4 \pm 1.5) \times 10^{-12}$	373		
$(5.0 \pm 1.5) \times 10^{-12}$	295	Sehested et al., 1997	PR-UVA (c)
<i>Branching Ratios</i>			
$k_1/k > 0.95$	296	Maricq et al., 1994	UVP-FTIR (d)
$k_2/k < 0.05$	296		

Comments

- Flash photolysis time-resolved UV absorption study of $\text{F}_2\text{-CF}_3\text{CH}_2\text{F-H}_2\text{-O}_2\text{-N}_2$ mixtures. The rate coefficients were obtained from a fit of the decay curves for CF_3CHFO_2 , HO_2 , CF_3O_2 and ROOH , based on a mechanism of 14 reactions.
- Flash photolysis of H_2O_2 in the presence of $\text{CF}_3\text{CH}_2\text{F-O}_2\text{-N}_2$ mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from CF_3CHFO_2 , HO_2 and CF_3O_2) were recorded in the wavelength range 220 nm to 240 nm. k derived from simulations of the decay traces using a 15 reaction mechanism.
- Pulse radiolysis study of $\text{CF}_3\text{CH}_2\text{F-H}_2\text{-O}_2\text{-SF}_6$ mixtures at a total pressure of 1013 mbar. Decays in transient absorption signals (with contributions from CF_3CHFO_2 , HO_2 and CF_3O_2) were recorded at 230 nm and 240 nm. The cited value of k was derived from simulation of the decay in absorption, using a 22 reaction chemical mechanism.
- Steady-state photolysis of $\text{Cl}_2\text{-CF}_3\text{CH}_2\text{F-H}_2\text{-O}_2\text{-N}_2$ mixtures with FTIR analysis of the products HC(O)F , $\text{CF}_3\text{C(O)F}$, C(O)F_2 and $\text{CF}_3\text{O}_3\text{CF}_3$. The branching ratio, k_2/k , cited above was based on measurements of CF_3COF , and the value of k_1/k was inferred.

Preferred Values

$k = 4.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.0 \times 10^{-13} \exp(910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 210-365 K.

$k_1/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

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

$\Delta(k_1/k) = {}^{+0.0}_{-0.1}$ at 298 K.

Comments on Preferred Values

The preferred value of k at 298 K is the average of the results of Maricq et al. (1994) (based on their Arrhenius expression), Hayman and Battin-Leclerc (1995) and Sehested et al. (1997). The results of these studies are in good agreement, even though k was necessarily extracted from simulations of complex systems. The preferred Arrhenius expression for k is based on the E/R value from the study of Maricq et al. (1994), combined with a pre-exponential factor adjusted to give the preferred value of k at 298 K. The results of Hayman and Battin-Leclerc (1995) at 323 K and 373 K are also consistent with this recommendation. The preferred branching ratios are based on those reported by Maricq et al. (1994), which require confirmation.

It is interesting to note that k is approximately a factor of two smaller than that recommended for the reaction of HO₂ with C₂H₅O₂. This confirms a deactivating influence of α -F and α -CF₃ groups, observed for the reactions of a number of halogenated peroxy radicals with HO₂.

References

- Hayman, G. and Battin-Leclerc, F.: J. Chem. Soc. Farad. Trans. 91, 1313, 1995.
Maricq, M. M., Szente, J. J., Hurley, M. D. and Wallington, T. J.: J. Phys. Chem. 98, 8962, 1994.
Sehested, J., Mogelberg, T., Fagerstrom, K., Mahmoud, G. and Wallington, T. J.: Int. J. Chem. Kinet. 29, 673, 1997.