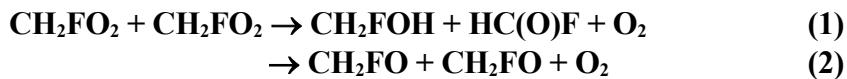


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx65

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This data sheet updated: 24th January 2006.



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>			
$k_{\text{obs}} = 3.3 \times 10^{-13} \exp[(700 \pm 100)/T]$	228-380	Dagaut et al., 1988	FP-UVA (a,b)
$k_{\text{obs}} = (3.07 \pm 0.65) \times 10^{-12}$	298		
$k_{\text{obs}} = (4.01 \pm 0.52) \times 10^{-12}$	298	Wallington et al., 1992	PR-UVA (a,c)
<i>Branching Ratios</i>			
$k_2/k > 0.77$	298	Wallington et al., 1992	UVP-FTIR (d)

Comments

- (a) k_{obs} is based on the measured overall second-order decay of CH_2FO_2 , defined by $-\frac{d[\text{CH}_2\text{FO}_2]}{dt} = 2k_{\text{obs}}[\text{CH}_2\text{FO}_2]^2$. As described in detail by Lesclaux (1997), HO_2 radicals formed from the subsequent chemistry of CH_2FO (formed from channel (2)) are expected to lead to secondary removal of CH_2FO_2 . The true value of k is expected to fall in the range $k_{\text{obs}}/(1+\alpha) < k < k_{\text{obs}}$, where $\alpha = k_2/k$.
- (b) Flash photolysis of Cl_2 in the presence of $\text{CH}_3\text{F}-\text{O}_2-\text{N}_2$ mixtures at total pressures of 33-533 mbar. CH_2FO_2 radicals were monitored by UV absorption with $\sigma_{240 \text{ nm}} = (3.72 \pm 0.45) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.
- (c) Pulse radiolysis study of $\text{CH}_3\text{F}-\text{O}_2-\text{SF}_6$ mixtures at a total pressure of 1000 mbar. CH_2FO_2 radicals were monitored by UV absorption with $\sigma_{240 \text{ nm}} = (4.11 \pm 0.67) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.
- (d) CH_2FO_2 radicals were generated from the steady-state photolysis of $\text{Cl}_2-\text{CH}_3\text{F}$ mixtures at 933 mbar pressure of air. The decay of CH_3F and the formation of products was monitored by FTIR spectroscopy. No CH_2FOH was observed within the detection limits of the apparatus. Significant amounts of HC(O)F were observed ($86 \pm 5\%$) and, in experiments with high conversions, CH_2FOOH was observed ($11 \pm 4\%$).

Preferred Values

$$k = 2.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.5 \times 10^{-13} \exp(700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220-380 \text{ K.}$$

$$k_2/k = 1.0 \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

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

$$\Delta(k_2/k) = {}^{+0.0}_{-0.2} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The product study of Wallington et al. (1992) showed no formation of CH₂FOH, suggesting that channel (1) is negligible at 298 K. The high yields of HC(O)F are also consistent with the dominance of channel (2), followed by reaction of CH₂FO with O₂ to form HC(O)F and HO₂. A more recent product study of the CH₂FO₂ + HO₂ reaction (Wallington et al., 1994) has shown that the only ca. 30% of that reaction produces CH₂FO₂H and O₂, with the remainder forming HC(O)F, H₂O and O₂. The low yields of CH₂FO₂H observed by Wallington et al. (1992) are thus partially explained by this, but also suggest that HO₂ is probably removed by its self reaction in competition with reaction with CH₂FO₂.

The preferred value of k at 298 K is derived from the k_{obs} values reported by Dagaut et al. (1988) and Wallington et al. (1992), adjusted to be consistent with the re-evaluation of $\sigma_{240 \text{ nm}}(\text{CH}_2\text{FO}_2) = 4.03 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ by Nielsen and Wallington (1997). Similar to a procedure adopted by Lesclaux (1997) for peroxy radicals for which the self reaction rate coefficients are \geq ca. $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, k is estimated to be $k_{\text{obs}}/(1+0.5(k_2/k))$, with this approximation assuming that the secondary reaction of HO₂ with CH₂FO₂ competes equally with its removal via HO₂ + HO₂. The reliability range reflects that k has been derived by this approximate procedure. The preferred value of E/R is based on the k_{obs} expression of Dagaut et al. (1988). This assumes that the above competition remains valid over the entire temperature range, consistent with the CH₂FO₂ and HO₂ self reactions, and reaction of CH₂FO₂ with HO₂ possessing similar temperature dependences.

References

- Dagaut, P., Wallington, T. J. and Kurylo, M.J.: Int. J. Chem. Kinet. 20, 815, 1988.
Lesclaux, R.: Combination of peroxy radicals in the gas phase. In 'Peroxy Radicals', edited by Z.B. Alfassi. John Wiley and Sons, 1997.
Nielsen, O. J. and Wallington, T.J.: Ultraviolet absorption spectra of peroxy radicals in the gas phase. In 'Peroxy Radicals', edited by Z.B. Alfassi. John Wiley and Sons, 1997.
Wallington, T. J., Ball, J. C., Nielsen, O. J. and Bartkiewicz, E.: J. Phys. Chem. 96, 1241, 1992.
Wallington, T. J., Hurley, M. D., Schneider, W. F., Sehested, J. and Nielsen, O. J.: Chem. Phys. Lett. 218, 34, 1994.