IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx70

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$$CF_3CHFO_2 + CF_3CHFO_2 \rightarrow CF_3COF + CF_3CHFOH + O_2 \quad (1)$$
$$\rightarrow CF_3CHFO + CF_3CHFO + O_2 \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$7.8 \times 10^{-13} \exp[(605 \pm 40)/T]$	211-372	Maricq and Szente, 1992	FP-UVA (a,b)
$(7 \pm 1.0) \times 10^{-12}$	297		
$(3.5 \pm 0.8) \times 10^{-12}$	295	Sehested et al., 1997	PR-UVA (a,c)
Branching Ratios			
$k_1/k = 0.14$	273	Wallington et al., 1992	UVP-FTIR (d)
$k_1/k = 0.08$	298		
$k_1/k = 0.05$	353		
$k_1/k = 0.055$	273	Tuazon and Atkinson, 1993	UVP-FTIR (e)
$k_1/k = 0.049$	298		
$k_1/k = 0.046$	320		

Comments

(a) k is defined by $-d[CF_3CHFO_2]/dt = 2k[CF_3CHFO_2]$.[2]

(b) Flash photolysis of F_2 in the presence of N_2, O_2, He and CF_3CH_2F. CF_3CHFO_2 radicals were monitored by UV absorption with $\sigma_{213\,nm} = (5.2 \pm 0.3) \times 10^{-13}$ cm^2 molecule^{-1}. The derived value of k listed above was obtained by modelling the decay curves for CF_3CFHO_2 radicals with a mechanism of 9 reactions.

(c) Pulse radiolysis study of CF_3CH_2F-O_2-SF_6 mixtures at a total pressure of 1000 mbar. CF_3O_2 radicals were monitored by UV absorption at 220 nm ($\sigma = 5.34 \times 10^{-18}$ cm^2 molecule^{-1}), 230 nm ($\sigma = 4.50 \times 10^{-18}$ cm^2 molecule^{-1}) and 240 nm ($\sigma = 3.06 \times 10^{-18}$ cm^2 molecule^{-1}). The cited value of k was derived from simulation of the decay in absorption, using a chemical mechanism in which secondary removal of CF_3CHFO_2 was explicitly represented.

(d) Steady-state photolysis of Cl_2 in the presence of CF_3CFH_2-O_2 mixtures at a total pressure of 933 mbar with FTIR analysis of the products HC(O)F and $CF_3C(O)F$. The branching ratio was determined from the yields of $CF_3C(O)F$ as a function of added O_2, extrapolated to zero O_2 partial pressure.

(e) Similar experiments to those of Comment (d). The branching ratios were derived from the yields of $CF_3C(O)F$ in the presence of 787 mbar N_2 and 1.3 mbar O_2.

Preferred Values

$k = 4.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.2 \times 10^{-13} \exp(605/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210-375 K.

$k_2/k = 0.93$, independent of temperature over the range 270-350 K.

$k_1/k = 0.07$, independent of temperature over the range 270-350 K.

Reliability

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

$\Delta(E/R) = \pm 200$ K.

$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.05$ over the temperature range 270-350 K.

Comments on Preferred Values

The preferred value of k at 298 K is the average of the results of Maricq and Szente (1992) (based on their Arrhenius expression) and Sehested et al. (1997). The preferred Arrhenius expression for k is based on the E/R value from the study of Maricq and Szente (1992), combined with a pre-exponential factor adjusted to give the preferred value of k at 298 K. The temperature dependence reported by Maricq and Szente (1992), is based on temperature-independent branching ratios k_1/k and k_2/k over the range 273-363 K. This is consistent with our recommendation of a temperature-independent branching ratio, k_1/k, which is the average of the experimental results of Wallington et al. (1992) and Tuazon and Atkinson (1993) over the range 273-353 K. The recommended value of k_2/k is inferred from that of k_1/k. It should be noted, however, that the results of Maricq and Szente (1992) for k at 216 K are not consistent with temperature-independent branching ratios.

The kinetics studies (Maricq and Szente, 1992; Sehested et al., 1997) report values of k at 298 K which differ by a factor of 1.7, and this is reflected in the assigned reliability range. Confirmation of both the overall rate coefficient and the branching ratios is required.

References

Maricq, M. M. and Szente, J. J.: J. Phys. Chem., 96, 10862, 1992.

Sehested, J., Mogelberg, T., Fagerstrom, K., Mahmoud, G. and Wallington, T. J.: Int. J. Chem. Kinet., 29, 673, 1997.

Tuazon, E. C. and Atkinson, R.: J. Atmos. Chem., 16, 301, 1993.

Wallington, T. J., Hurley, M. D., Ball, J. C. and Kaiser, E. W.: Environ. Sci. Technol., 26, 1318, 1992.