IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx67

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$$CF_3O_2 + CF_3O_2 \rightarrow CF_3O + CF_3O + O_2$$
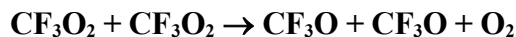
$\Delta H° = -83.2 \text{ kJ mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.8 \pm 0.5) \times 10^{-12}$	295	Nielsen et al., 1992	PR-UVA (a)
1.8×10^{-12}	298	Maricq and Szente, 1992a	FP-UVA (b)
$(1.8 \pm 0.5) \times 10^{-12}$	297	Maricq and Szente, 1992b	FP-UVA (c)
$(1.2 \pm 0.3) \times 10^{-12}$	298	Biggs et al., 1997	DF-LIF/MS (d)
$(2.25 \pm 0.3) \times 10^{-12}$	295	Sehested et al., 1997	PR-UVA (e)

Comments

(a) Pulse radiolysis study of CHF$_3$-O$_2$-SF$_6$ mixtures at a total pressure of 1000 mbar. CF$_3$O$_2$ radicals were monitored by UV absorption with $\sigma_{230 \text{ nm}} = (2.06 \pm 0.40) \times 10^{-18}$ cm^2 molecule^{-1}, and an observed rate coefficient, $k_{obs} = (3.6 \pm 0.9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, was derived from the decay in absorption. Associated FTIR product studies using the photolysis of F$_2$-CHF$_3$-O$_2$-N$_2$ mixtures demonstrated quantitative formation of CF$_3$OOOCF$_3$, which was explained by the secondary reaction of CF$_3$O with CF$_3$O$_2$. The cited value of k is thus $0.5k_{obs}$, to take account of this secondary loss of CF$_3$O$_2$.

(b) Flash photolysis of CHF$_3$-F$_2$-O$_2$ mixtures with time-resolved absorption spectroscopy for the detection of CF$_3$O$_2$ radicals, with $\sigma_{210 \text{ nm}} = (4.3 \pm 0.3) \times 10^{-18}$ cm^{-2} molecule^{-1}. A value of $k_{obs} = (3.1 \pm 0.25) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} was determined from the time-dependence of the CF$_3$O$_2$ radical absorbance. The cited value of k was obtained from a simulation in which secondary removal of CF$_3$O$_2$ was explicitly represented.

(c) Flash photolysis of F$_2$ in the presence of N$_2$, O$_2$, He, and CF$_3$CFH$_2$. Secondary generation of CF$_3$O$_2$ in the system occurred by the reaction CF$_3$CHFO → CF$_3$ + HCOF, followed by CF$_3$ + O$_2$ + M → CF$_3$O$_2$ + M. CF$_3$O$_2$ radicals were monitored by UV absorption, and the 298 K value of $k_{obs} = 3.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, derived in the authors' previous study (Maricq and Szente, 1992a), was shown to provide a good description of the time dependence of the formation and removal of CF$_3$O$_2$. The previous value (Maricq and Szente, 1992a) of the rate coefficient for the elementary reaction, k, was therefore confirmed and assigned the cited error limits. Additional measurements suggested that k_{obs} decreases with increasing temperature.

(d) Experiments performed at pressures in the range 1.3 to 4 mbar. CF$_3$O$_2$ radicals were produced by the F + CHF$_3$ reaction or the F + CF$_3$I reaction, with subsequent addition of O$_2$. CF$_3$O$_2$ radicals were monitored by titration to NO$_2$ following reaction with excess NO, with detection of NO$_2$ by either LIF or MS. An observed rate coefficient, $k_{obs} = (2.0 \pm 1.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, was derived from the decay in CF$_3$O$_2$. The cited value of k was obtained from a simulation in which secondary removal of CF$_3$O$_2$ was explicitly considered.

(e) Pulse radiolysis study of CHF$_3$-O$_2$-SF$_6$ mixtures at a total pressure of 1000 mbar. CF$_3$O$_2$ radicals were monitored by UV absorption with $\sigma_{230 \text{ nm}} = 3.43 \times 10^{-18}$ 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_3O_2 was explicitly represented.

Preferred Values

$k = 1.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

   The reported quantitative formation of CF_3OOOCF_3 from CHF_3 oxidation, in the product study of Nielsen et al. (1992) is consistent with the self-reaction of CF_3O_2 proceeding via formation of CF_3O radicals, which react exclusively with CF_3O_2.

   The five reported values of k are in reasonable accord, covering a range of approximately two. The discharge-flow determination of Biggs et al. (1997) lies at the low end of the range, and this may be indicative a pressure dependence of the reaction. Biggs et al. (1997) performed QRRK calculations, based on the reaction proceeding via a $[CF_3O_4CF_3]^*$ intermediate and estimated that the high pressure limiting k (achieved at ca. 35-70 mbar) is ca. 15% greater than their measured value, i.e. $(1.4 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The observed range in reported k values may also be reduced by re-evaluating the results of the UV absorption studies (Nielsen et al., 1992; Maricq and Szente, 1992a,b; Sehested et al., 1997) using the recommended CF_3O_2 absorption cross sections reported by Nielsen and Wallington (1997), which are somewhat lower than those applied by Maricq and Szente (1992a,b) and Sehested et al. (1997). This leads to respective revised values of k of 1.5×10^{-12} and 1.4×10^{-12} cm^3 molecule^{-1} s^{-1} in those studies, and a much improved general agreement among the reported studies. The preferred value of k is therefore based on the re-evaluations of the UV absorption studies and the estimated high pressure value of Biggs et al. (1997). Maricq and Szente (1992b) obtained limited evidence that k_{obs} possesses a weak negative temperature coefficient, but further temperature dependence studies are required to quantify this.

References

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Nielsen, O. J., Ellermann, T., Sehested, J., Bartkiewiecz, E., Wallington, T. J. and Hurley, M. D.: Int. J. Chem. Kinet., 24, 1009, 1992.
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