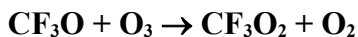


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx40

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.



$$\Delta H^\circ = -101.1 \text{ kJ mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$<1 \times 10^{-13}$	295	Nielsen and Sehested, 1993	PR/UVA(a)
$<5 \times 10^{-14}$	210-353	Maricq and Szente, 1993	FP/UVA(b)
$<2 \times 10^{-15}$	298	Fockenberget al., 1994	LP/LIF(c)
$<4 \times 10^{-14}$	298	Ravishankara et al., 1994	FT/CIMS(d)
$(2.5 \pm 0.7) \times 10^{-14}$	298	Turnipseed et al., 1994	PLP/LIF(e)
$(3.7 \pm 1.5) \times 10^{-14}$	373		
$(2.8 \pm 0.5) \times 10^{-15}$	298	Mellor and Moortgat, 1995	(f)
$(1.3 \pm 0.5) \times 10^{-14}$	298	Bourbon et al., 1996	FT/LIF(g)
<i>Relative Rate Coefficients</i>			
$<3 \times 10^{-14}$	295	Wallington et al., 1993	RR(h)
$(1.5 \pm 0.5) \times 10^{-14}$	296	Wallington and Ball, 1995	(i)

Comments

- Radicals generated by pulse radiolysis of $\text{CHF}_3\text{-O}_2\text{-O}_3\text{-SF}_6$ mixtures. Upper limit for k derived from simulations of ozone absorption transients at 254 nm and 276 nm in the presence of CF_3O and CF_3O_2 radicals.
- Radicals generated by 351 nm photolysis of F_2 in a flowing $\text{F}_2\text{-CHF}_3\text{-O}_3\text{-O}_2\text{-N}_2$ mixture. O_3 and CF_3O_2 radicals were monitored by absorption at 255 nm and 210 nm respectively.
- CF_3O radicals were generated by excimer laser photolysis of CF_3OCl at 351 nm.
- CF_3O radicals were generated by pyrolysis of CF_3OOCF_3 .
- CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.
- Static photolysis of CF_3OOCF_3 in the presence of O_3 ; Analysis of CF_3O and $\text{CF}_3\text{OO}_3\text{CF}_3$ products by FTIR. k determined by analysis of complex mechanism.
- CF_3O radicals were generated by pyrolysis of CF_3OOCF_3 .
- Radicals generated by visible photolysis of $\text{CF}_3\text{NO/O}_3$ mixtures in 700 torr O_2 . Analysis was by FTIR spectrometer. Value of k was derived by authors from the measured ratio $k/k(\text{CF}_3\text{O} + \text{NO}_2)$ and an estimated value of $k(\text{CF}_3\text{O} + \text{NO}_2)$.
- Relative rate technique using FTIR. k measured relative to $k(\text{CF}_3\text{O} + \text{CH}_4) = 2.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).

Preferred Values

$$k = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2 \times 10^{-12} \exp(-1400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{-}370 \text{ K.}$$

Reliability

$\Delta \log k = \pm 1$ at 298 K.

$\Delta(E/R) = \pm 600$ K.

Comments on Preferred Values

The preferred value of k at 298 K is an average of the room temperature results of Turnipseed et al. (1994), Wallington and Ball (1995) and Bourbon et al (1996). Fockenberg et al. (1994) and Meller and Moortgat (1995) reported room temperature values an order of magnitude lower. The reason for this discrepancy is unknown, although both studies appear to have possibilities for interference by secondary chemistry. Upper limits reported in the studies of Nielsen and Sehested (1993), Maricq and Szenté (1993), Ravishankara et al. (1994) and Wallington et al. (1993) are all consistent with the recommendation. Because of the large uncertainties in the two values of Turnipseed et al. (1994), Arrhenius parameters have not been derived using these values. Rather, the recommended A factor has been estimated by analogy with other CF_3O reactions, and the value of E/R fitted to the preferred room temperature value.

References

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