

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet III.A1.6 iFOx6

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$$\Delta H^\circ = -54.0 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$5.2 \times 10^{-34} \exp(656/T)$ [He]	272-362	Zetzsch, 1973	DF-MS (a)
4.7×10^{-33} [He]	298		
$(7 \pm 2) \times 10^{-33}$ [He]	293	Arutyunov, Popov and Chaikin, 1976	DF-EPR
$(1.4 \pm 0.4) \times 10^{-32}$ [N ₂]	293		(b)
$(6 \pm 2) \times 10^{-33}$ [Ar]	293		
$(5.4 \pm 0.6) \times 10^{-33}$ [He]	298	Chen et al., 1977	FP (c)
$(1.5 \pm 0.3) \times 10^{-32}$ [O ₂]	298		
$(5.0 \pm 0.6) \times 10^{-33}$ [F ₂]	298		
$(8.4 \pm 0.9) \times 10^{-33}$ [Ar]	298		
$2.8 \times 10^{-34} \exp(906/T)$ [Ar]	223-293	Shamonima and Kotov, 1979	DF-EPR
$(6.1 \pm 1.8) \times 10^{-33}$ [Ar]	293		(d)
$(1.0 \pm 0.3) \times 10^{-32}$ [O ₂]	298	Chebotarev, 1979	PLP (e)
$(3.2 \pm 2.1) \times 10^{-33}$ [Ar]	298	Smith and Wrigley, 1980	(f)
$(3.7 \pm 2.4) \times 10^{-33}$ [Ar]	298	Smith and Wrigley, 1981	(f)
$(4.3 \pm 0.4) \times 10^{-33} (T/300)^{-1.6}$ [Ar]	295-359	Pagsberg et al., 1987	PR (g)
$(2.8 \pm 0.2) \times 10^{-33}$ [He]	298	Lyman and Holland, 1988	PLP (h)
$(3.1 \pm 0.2) \times 10^{-33}$ [Ar]	298		
1.4×10^{-32} [SF ₆]	295	Ellermann et al., 1994	PR (i)
$5.8 \times 10^{-33} (T/300)^{-1.7}$ [N ₂]	100-373	Campuzano-Jost et al., 1995	PLP (j)

Comments

- (a) Detection of F atoms and FO₂ radicals.
 (b) Detection of F atoms.
 (c) Detection of vibrationally excited HF by IR chemiluminescence.
 (d) Detection of F atoms in the presence of excess O₂ and Ar. Experimental conditions were varied over only limited ranges; for example, [O₂] was varied by a factor of 2 and the total pressure was fixed. The third-order rate coefficient reported for Ar as the diluent gas may be somewhat overestimated as the O₂ ranged from ~12% to ~25% of the total pressure. The stoichiometry was assumed to be 2 (*i.e.*, $-\text{d}[\text{F}]/\text{dt} = 2k[\text{F}][\text{O}_2][\text{M}]$) due to secondary removal of atomic fluorine by reaction with the primary product FO₂.

- (e) Photolysis of WF₆-H₂-O₂-He mixtures at ~200 nm, with detection of HF by IR chemiluminescence. The relative efficiencies of M were reported to be O₂:Ar = 1.4:1.0.
- (f) Laser photolysis of F₂/HCl/Ar mixtures in the presence of O₂ at pressures of 100-150 mbar. Vibrational chemiluminescence of HF monitored.
- (g) Experiments were carried out in Ar-F₂-O₂ mixtures with detection of FO₂ by absorption at 220 nm. The rate coefficient and the equilibrium constant were determined by varying the O₂ concentration. A value of $\Delta H^\circ(298\text{ K}) = -52.8\text{ kJ mol}^{-1}$ was derived.
- (h) Photolysis of F₂ at 248 nm in the presence of O₂ and bath gases. The reaction mechanism with 6 reactions was followed via the analysis of transient absorption signals at 215 nm. The forward and backward rate coefficients of the reactions $F + O_2 + M \rightarrow FO_2 + M$ and $F + FO_2 + M \rightarrow F_2O_2 + M$ were determined. A value of $\Delta H^\circ(298\text{ K}) = -(56.4 \pm 1.7)\text{ kJ mol}^{-1}$ was derived.
- (i) Experiments with SF₆-O₂ mixtures at 0.20-1.0 bar total pressure with kinetic UV spectroscopic detection of FO₂ radicals between 215 and 254 nm. Falloff extrapolations were made with $F_c = 0.6$.
- (j) FO₂ radicals were detected by UV absorption. Experiments were carried out at total pressures up to 1000 bar of the bath gases He, Ar, and N₂. Measurements of the equilibrium constant lead to $\Delta H^\circ(0\text{ K}) = -49.8\text{ kJ mol}^{-1}$. Falloff extrapolations were made with F_c near 0.5.

Preferred Values

$$k_0 = 5.8 \times 10^{-33} (T/300)^{-1.7} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 100\text{-}380\text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at } 298\text{ K.}$$

$$\Delta n = \pm 0.5.$$

Comments on Preferred Values

Because of the large data-base from the study of Campuzano-Jost et al. (1995), their rate coefficients values are preferred and are in reasonable agreement with earlier work. Falloff curves were constructed with F_c near 0.5.

High-pressure rate coefficients Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
2.0×10^{-12}	295	Ellermann et al., 1994	PR (a)
1.2×10^{-10}	100-373	Campuzano-Jost et al., 1995	PLP (b)

Comments

- (a) See comment (h) for k_0 .
 (b) See comment (i) for k_0 .

Preferred Values

$k_{\infty} = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 100-380 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.3$ over the temperature range 100-380 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

Because of the large pressure range studied by Campuzano-Jost et al. (1995), a reliable falloff extrapolation towards k_{∞} was possible. The data of Campuzano-Jost et al. (1995) are therefore preferred together with values of F_c near 0.5.

The following text-line combines the preferred values for the high and low pressure limiting rate coefficients to generate a single, cut-and-paste expression for calculation of k :

$$= ((5.8e-33*(T/300)^{-1.7}*M*(1.2e-10))/((5.8e-33*(T/300)^{-1.7}*M+(1.2e-10))*10^{(\log_{10}(0.5)/(1+(\log_{10}((5.8e-33*(T/300)^{-1.7}*M/(1.2e-10))/(0.75-1.27*\log_{10}(0.5))))^2)})$$

The molecular density, $M = 7.243 \times 10^{21} P(\text{bar})/T(\text{K})$

Intermediate Falloff Range Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	P/Torr	M	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate coefficients</i>					
2.4×10^{-13}	600 mbar	SF ₆	298	Wallington and Nielsen, 1991	PR (a)
$(2.35 \pm 0.2) \times 10^{-13}$	600 mbar	SF ₆	298	Wallington et al., 1992	PR (b)

Comments

- (a) Experiments were carried out in mixtures of SF₆ and O₂ (6.1-20 mbar). FO₂ radicals were monitored by UV absorption at 220 nm.
- (b) Experiments were carried out in mixtures of SF₆ and O₂ (2.5-15 mbar). FO₂ radicals were monitored by UV absorption at 220 nm. The results were analyzed together with those of Lyman and Holland (1988).

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