

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iFOx7

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 re-transmitted or disseminated either electronically or in hard copy without explicit written permission.

This data sheet updated: 9th March 2005.



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

Low-pressure rate coefficients Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1.8×10^{-17} [Ar]	295	Pagsberg et al., 1987	PR (a)
3.1×10^{-17} [Ar]	312.5		
2.8×10^{-16} [Ar]	359		
$(2.5 \pm 1.0) \times 10^{-18}$ [He]	298	Lyman and Holland, 1988	PLP (b)
$1.0 \times 10^{-5} T^{1.25} \exp(-5990/T)$ [N ₂]	315-420	Campuzano-Jost et al., 1995	PLP (c)
1.5×10^{-17} [N ₂]	298		

Comments

- Experiments were carried out in Ar-F₂-O₂ mixtures with detection of FO₂ by absorption at 220 nm. The rate of approach to equilibrium was monitored and the equilibrium constant measured. A value of $\Delta H^\circ(298 \text{ K}) = 52.8 \text{ kJ mol}^{-1}$ was derived by a third-law analysis.
- Photolysis of F₂ at 248 nm in the presence of O₂ and bath gases. Transient absorptions at 215 nm were monitored and the approach to equilibrium was analyzed. A value of $\Delta H^\circ(298 \text{ K}) = 56.4 \text{ kJ mol}^{-1}$ was derived.
- The kinetics were followed by monitoring the FO₂ radical by UV absorption. Experiments were carried out between 100 K and 375 K at total pressures between 1 bar and 1000 bar, and in 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 carried out with a value of F_c near 0.5. The expression for k_0 was derived from the recombination rate coefficients of the reverse reaction and the equilibrium constants.

Preferred Values

$$k_0 = 1.5 \times 10^{-17} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 8.4 \times 10^{-9} (T/300)^{-1.25} \exp(-5990/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 310\text{-}420 \text{ K.}$$

Reliability

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

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

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The results of Campuzano-Jost *et al.*³ are in reasonable agreement with those of Pagsberg *et al.* (1987), but differ at 298 K by a factor of 6 with the data from Lyman and Holland (1988). The preferred values are based on the data of Campuzano-Jost *et al.* (1995).

High-pressure rate coefficients Rate coefficient data

k_{∞}/s^{-1}	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.3 \times 10^{13} T^{0.45} \exp(-5990/T)$	315-420	Campuzano-Jost <i>et al.</i> , 1995	PLP (a)

Comments

(a) See comment (c) for k_0 .

Preferred Values

$k_{\infty} = 3.1 \times 10^5 \text{ s}^{-1}$ at 298 K.

$k_{\infty} = 1.7 \times 10^{14} (T/300)^{0.45} \exp(-5990/T) \text{ s}^{-1}$ over the temperature range 310-420 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.5$.

$\Delta(E/R) = \pm 500 \text{ K}$.

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 F_c values near 0.5.

References

- Campuzano-Jost, P., Croce, A. E., Hippler, H., Siefke, M. and Troe, J.: *J. Chem. Phys.*, 102, 5317, 1995.
- Lyman, J. L. and Holland, R.: *J. Phys. Chem.*, 92, 7232, 1988.
- Pagsberg, P., Ratajczak, E., Sillesen, A. and Jodkowski, J. T.: *Chem. Phys. Lett.*, 141, 88, 1987.