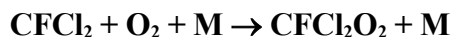


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx84

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: 5th July 2005.



$$\Delta H^\circ = -124.6 \text{ kJ mol}^{-1}$$

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>			
$(5.0 \pm 0.8) \times 10^{-30} [\text{N}_2]$	298	Caralp and Lesclaux, 1983	PLP-MS (a)
$5.5 \times 10^{-30} (T/298)^{-6} [\text{N}_2]$	233-373	Danis, 1991	PLP-MS (b)

Comments

- (a) Pulsed laser photolysis–MS study. Falloff curve measure over the range 0.3-16 mbar, extrapolated with $F_c = 0.6$ and $k_\infty = 6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (b) As comment (a). Results cited and evaluated by Forst and Caralp (1991).

Preferred Values

$$k_0 = 6 \times 10^{-30} (T/298)^{-6} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 230-380 K.}$$

Reliability

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

$$\Delta n = \pm 3.$$

Comments on Preferred Values

These are the only measurements, from a single laboratory, which were made close to the low pressure limit of the falloff curve. Using F_c values of 0.35-0.4 such as observed for $\text{CCl}_3 + \text{O}_2$ and $\text{CF}_3 + \text{O}_2$ would only slightly modify the extrapolated values of k_0 , but be of larger influence on k_∞ .

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>			
$(6 \pm 1) \times 10^{-12}$	298	Caralp and Lesclaux, 1983	PLP-MS (a)
$(9 \pm 3) \times 10^{-12}$	233-273	Danis, 1991	PLP-MS (b)

Comments

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

Preferred Values

$k_\infty = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230-300 K.

Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Values

See Comments on Preferred Values for k_0 . Using $F_c = 0.4$ instead of 0.6 in the present case would increase k_∞ by a factor of 1.5. The present choice, therefore, is based on the data from Caralp and Lesclaux (1983) and $F_c \approx 0.4$.

References

- Caralp, F. and Lesclaux, R.: Chem. Phys. Lett., 102, 54, 1983.
- Danis, F.: Ph. Thesis, Bordeaux 1990, cited by Forst and Caralp (1991).
- Forst, W. and Caralp, F.: J. Chem. Soc. Faraday Trans., 87, 2307, 1991.