IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx4

This data sheet updated: 7th June 2007.

$O + OClO + M \rightarrow ClO_3 + M$

$\Delta H° = -126.6$ kJ·mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.4 \pm 0.3) \times 10^{-31}$ [Ar]	298	Colussi, 1990	PLP-RF (a)
$1.9 \times 10^{-31} (T/298)^{-1.1}$ [Ar]	248-312	Colussi, Sander and Friedl, 1992	PLP-RF (b)

Comments

(a) Pulsed laser photolysis of OClO at pressures of Ar between 10 and 1000 mbar. The oxygen atoms produced were detected by resonance fluorescence. Fit of the falloff curve used F_c = 0.6.

(b) See comment (a). The falloff curves were fitted with F_c = 0.5 at 248 K, 0.48 at 273 K, and 0.45 at 312 K.

Preferred Values

$k_0 = 1.9 \times 10^{-31} (T/298)^{-1}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 240-320 K.

Reliability

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

$\Delta n = \pm 0.5$ K.

Comments on Preferred Values

The preferred values are based on the data of Colussi et al. (1992) using falloff extrapolations with a fitted value of F_c = 0.5 at 298 K. Low pressure experiments by Gleason et al. (1994) (1.3-7 mbar) indicate the presence of the reaction $O + OClO \rightarrow ClO + O_2$.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(3.1 ± 0.8) x 10^{-11}	298	Colussi, 1990	PLP-RF (a)
2.8 x 10^{-11}	248-312	Colussi, Sander and Friedl, 1992	PLP-RF (b)

Comments

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

Preferred Values

k_∞ = 2.8 x 10^{-11} cm^3 molecule^{-1} s^{-1} over the temperature range 240-320 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

See comments on k_0. The rate coefficients of Colussi et al. (1992) were confirmed by measurements carried out by Mauldin et al. (1997) at 260 K and 430 mbar of N_2. Under these conditions (260 K and 430 mbar of N_2), Mauldin et al. (1997) observed that the reaction led to the formation of ClO radicals with a yield of <5%. Mauldin et al. (1997) concluded that the combination reaction may involve the intermediate formation of a species such as O·OClO which is different from ClO_3 and which does not rearrange to give O_2 + ClO.

Theoretical modelling of the reaction by Zhu and Lin (2002) led to values of k_∞ which were a factor of 5-7 higher than obtained from the measurements. As the measurements (Colussi et al., 1992) look well-behaved; they are preferred to the modeling. There is also still some dispute about the heat of reaction, see the calculations by Sicre and Cobos (2003).

References

Colussi, A. J.: J. Phys. Chem., 94, 8922, 1990.
Colussi, A. J., Sander, S. P. and Friedl, R. R.: J. Phys. Chem., 96, 4442, 1992.
Gleason, J. F., Nesbitt, F. L. and Stief, L. J.: J. Phys. Chem., 98, 126, 1994.
Mauldin III, R. L., Burkholder, J. B. and Ravishankara, A. R.: Int. J. Chem. Kinet., 29, 139, 1997.
Sicre, J. E. and Cobos, C. J.: J. Mol. Struct. (Theochem), 620, 215, 2003.
Zhu, R. S. and Lin, M. C.: J. Phys. Chem., A 106, 8386 (2002).