IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet III.A2.52 iClOx37

This data sheet last evaluated March 2005.

$ClO + OClO + M \rightarrow Cl_2O_3 + M$

$\Delta H° = -43.2$ 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			
2.8×10^{-31} [N_2]	226	Parr et al., 1990	MM-UVA (a)
$(6.2 \pm 1.0) \times 10^{-32}(T/300)^{-4.7}$ [N_2]	200-260	Burkholder et al., 1993	PLP-UVA (b)

Comments

(a) Experiments carried out with Cl_2-OClO-N_2 mixtures in the pressure range 6.4-39 mbar. ClO monitored at 277.2 nm. The reaction was apparently close to the low pressure limit.

(b) Pulsed laser photolysis of mixtures of N_2O-Cl_2-OClO-He or CF_2Cl_2-OClO-N_2 at 193 nm. From the first mixture, rate data were obtained while from the second mixture equilibrium constants and the absorption spectra of Cl_2O_3 between 220 nm and 320 nm were derived. From a second-law analysis of the data, together with those of Hayman and Cox (1989), $\Delta H° = -(46.4 \pm 5.1)$ kJ mol^{-1} and $\Delta S° = -(88.7 \pm 18.9)$ J mol^{-1} K^{-1} were derived. The kinetic data were obtained from a fit of the falloff curves between 33 mbar and 333 mbar total pressure using $F_c = 0.6$

Preferred Values

$k_0 = 6.2 \times 10^{-32} (T/300)^{-4.7}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K.

Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Values

The values of the extensive study of Burkholder et al. (1993) are adopted here. At 226 K the rate coefficient of Parr et al. (1990) is in reasonable agreement with our preferred value (and therefore with the data of Burkholder et al., 1993). Ab-initio calculations from Clark and Francisco (1997) predict the more stable structure of Cl_2O_3 to be ClOCl(O)O and result in a value of the enthalpy of the recombination reaction of -45.6 kJ mol^{-1}.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(2.4 ± 1.2) x 10^{-11}	200-260	Burkholder et al., 1993	(a)

Comments

(a) See comment (b) for k_0.

Preferred Values

k_∞ = 2.4 x 10^{-11} cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200-300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200-300 K.

Comments on Preferred Values

The preferred values are from Burkholder et al. (1993). The falloff extrapolation was done with $F_c = 0.6$.

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:

=((6.2e-32*(*T*/300)^-4.7)*M*(2.4e-11))/((6.2e-32*(*T*/300)^-4.7)*M+(2.4e-11))*10^(log10(0.6)/(1+(log10((6.2e-32*(*T*/300)^-4.7)*M/(2.4e-11))/(0.75-1.27*log10(0.6)))^2))

The molecular density, M = 7.243×10^{21}P(bar)/T(K)

References

Burkholder, J. B., Mauldin III, R. L., Yokelson, R. J., Solomon, S., and Ravishankara, A. R.: J. Phys. Chem., 97, 7597, 1993.

Clark, J. and Francisco, J. S.: J. Phys. Chem. A, 101, 7145, 1997.

Hayman, G. D. and Cox, R. A.: Chem. Phys. Lett., 155, 1, 1989.

Parr, A. D., Wayne, R. P., Hayman, G. D., Jenkin, M. E. and Cox, R. A.: Geophys. Res. Lett., 17, 2357, 1990.