IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet III.A2.51 iClOx36

This data sheet last evaluated March 2005.

$Cl_2O_2 + M \rightarrow ClO + ClO + M$

$\Delta H° = 75.7$ 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			
$9.81 \times 10^{-7} \exp[-(7980 \pm 320)/T]$ $[N_2]$	260-310	Nickolaisen, Friedl and Sander, 1994	FP-UVA (a)
2.30×10^{-18} $[N_2]$	298		

Comments

(a) Photolysis of Cl_2 at λ >300 nm in the presence of Cl_2O. ClO radicals were monitored with an optical multichannel analyzer at 270 nm to 280 nm. The pressure range used was 33 mbar to 400 mbar. Dissociation rate coefficients and equilibrium constants determined from analysis of two stages of ClO decay. From a third-law analysis, a value of $\Delta H° = (75.7 \pm 0.9)$ kJ mol^{-1} was derived. A value of the equilibrium constant $K_C = (1.24 \pm 0.18) \times 10^{-27} \exp\{8820/T\}$ cm^3 molecule^{-1} was obtained in good agreement with a determination by Cox and Hayman (1988).

Preferred Values

$k_0 = 2.3 \times 10^{-18}$ $[N_2]$ s^{-1} at 298 K.
$k_0 = 3.7 \times 10^{-7} \exp(-7690/T)$ $[N_2]$ s^{-1} over the temperature range 260-310 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 900$ K.

Comments on Preferred Values

The preferred values are based on the preferred values for the reverse reaction and the equilibrium constant from Nickolaisen et al. (1994) which agrees very well with the results of Cox and Hayman (1988).

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
4.8 x 10^{15} exp(-8820/T)	260-310	Nickolaisen, Friedl and Sander, 1994	FP-UVA (a)
6.7 x 10^2	298		

Comments

(a) See comment (a) for k_0. Falloff curve constructed with $F_c = 0.6$.

Preferred Values

$k_\infty = 1.1 \times 10^3$ s^{-1} at 298 K.
$k_\infty = 1.8 \times 10^{14} \exp(-7690/T)$ s^{-1} over the temperature range 260-310 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are based on the preferred values for the reverse reaction and the equilibrium constant from Nickolaisen et al. (1994). Falloff curves are constructed with $F_c = 0.45$ like for the reverse reaction. One should keep in mind, however, that only data at $P < 1$ bar are represented. There is ample evidence that the reaction is governed by a superposition of the energy transfer and the radical-complex mechanism such that the chosen simple representation of the falloff curve does not apply rigorously.

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:

=((3.7e-7*exp(-7690/*T*))*M*(1.8e14*exp(-7690/*T*)))/((3.7e-7*exp(-7690/*T*))*M+(1.8e14*exp(-7690/*T*)))*10^(log10(0.45)/(1+(log10((3.7e-7*exp(-7690/*T*))*M/(1.8e14*exp(-7690/*T*)))/(0.75-1.27*log10(0.45)))^2))

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

References

Cox, R. A. and Hayman, G. D.: Nature, 332, 796, 1988.
Nickolaisen, S. L., Friedl, R. R. and Sander, S. P.: J. Phys. Chem., 98, 155, 1994.