IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx11

This data sheet updated: 9th March 2005.

$ClOO + M \rightarrow Cl + O_2 + M$

$\Delta H° = 23.8$ kJ·mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.9 x 10^{-14} [O_2]	185.4	Nicovich et al., 1991	PLP-RF (a)
2.8 x 10^{-10} exp(-1820/T) [N_2]	160-260	Baer et al., 1991	PLP-UVA
6.2 x 10^{-13} [N_2]	298*		(a)
6.3 x 10^{-10} exp(-2030/T) [O_2]	160-260	Baer et al., 1991	PLP-UVA
1.1 x 10^{-14} [O_2]	185.4		(a)

Comments

(a) From measurements of the reverse reaction and the equilibrium constant.

Preferred Values

$k_0 = 6.2 \times 10^{-13}$ [N_2] s^{-1} at 298 K.
$k_0 = 2.8 \times 10^{-10}$ exp(-1820/T) [N_2] s^{-1} over the temperature range 160-300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values are based on the extensive data of Baer et al. (1991). No deviations from third-order behavior were observed at pressures below 1 bar. The reaction probably does not proceed via an energy-transfer mechanism (see comments on the reverse reaction $Cl + O_2 + M \rightarrow ClOO + M$), but rather by a radical-complex mechanism.

References

Baer, S., Hippler, H., Rahn, R., Siefke, M., Seitzinger, N. and Troe, J.: J. Chem. Phys., 95, 6463, 1991.
Nicovich, J. M., Kreutter, K. D., Shackelford, C. J. and Wine, P. H.: Chem. Phys. Lett., 179, 367, 1991.