IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx30

This data sheet updated: 25th September 2003.

$$\mathbf{ClO + O_3 \rightarrow ClOO + O_2} \qquad \mathbf{(1)}$$
$$\mathbf{\rightarrow OClO + O_2} \qquad \mathbf{(2)}$$

$\Delta H°(1) = -146.8$ kJ·mol^{-1}
$\Delta H°(2) = -149.7$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$k_2 < 1 \times 10^{-18}$	298	DeMore et al., 1975	DF-MS
$k_2 < 1 \times 10^{-18}$	298	Wongdontri-Stuper et al., 1979	FP-UVA (a)
$k_1 < 1.3 \times 10^{-17}$	233	Stevens and Anderson, 1990	(b)
$k_1 < 1.4 \times 10^{-17}$	298		
$k_1 = (4.0 \pm 2.0) \times 10^{-16}$	413		

Comments

(a) Flash photolysis of Cl_2-O_3 mixtures. Upper limit to the rate coefficient obtained expected to really refer to k_2 (Stevens and Anderson, 1990).

(b) Discharge flow system. Reaction channel (1) was followed by monitoring ClO produced from the thermal decomposition of the product ClOO in the presence of O_3. The product ClO was distinguished from the reactant ClO through isotopic labelling.

Preferred Values

$k_1 < 1.5 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 < 1 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit for k_1 is based on the results of the study of Stevens and Anderson (1990). The preferred upper limit for k_2 is based on the data of DeMore et al. (1975) and Wongdontri-Stuper et al. (1979). The upper limit of Stevens and Anderson (1990) at room temperature can be combined with their measured rate coefficient at 413 K to derive $A_1 = 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $E_1/R > 3600$ K. For k_2 one can estimate $A_2 = 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and derive $E_2/R > 4000$ K.

References

DeMore, W. B., Lin, C. L. and Jaffe, S.: presented at ACS National Meeting, Philadelphia, PA, 1975.
Stevens, P. S. and Anderson, J. G.: Geophys. Res. Lett. 17, 1287, 1990.
Wongdontri-Stuper, W., Jayanty, R. K. M., Simonaitis, R. and Heicklen, J.: J. Photochem. 10, 163, 1979.