

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx42

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$$\Delta H^\circ = -71.2 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$< 1 \times 10^{-19}$	195-217	DeMore and Tschuikow-Roux, 1990	(a)

Comments

- (a) Photolysis ($\lambda > 300 \text{ nm}$) of $\text{Cl}_2\text{-O}_3$ or $\text{Cl}_2\text{-Cl}_2\text{O}$ mixtures, both in the gas phase and in the cryogenic solvents CF_4 , CO_2 and N_2O . The quantum yield of O_3 loss was measured.

Preferred Values

$$k < 1 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 200 \text{ K.}$$

Comments on Preferred Values

The recommended upper limit to the rate coefficient is that determined by DeMore and Tschuikow-Roux (1990) from measurements of the quantum yield of O_3 loss in the photolysis of $\text{Cl}_2\text{-O}_3$ mixtures at $\lambda > 300 \text{ nm}$. The experiments were very sensitive to this reaction. Reaction at a rate greater than this upper limit would have had a marked effect on the quantum yield of ozone loss and also would have resulted in a dependence of the quantum yield on the ozone concentration; however, neither effect was observed (DeMore and Tschuikow-Roux, 1990). These measurements refer to a temperature of about 200 K; the value of this rate coefficient at higher temperatures would be of no atmospheric significance because of the thermal decomposition of the Cl_2O_2 dimer.

References

DeMore, W. B. and Tschuikow-Roux, E.: J. Phys. Chem. 94, 5856, 1990.