

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx3

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$$\Delta H^\circ = -242.2 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(5 \pm 2) \times 10^{-13}$	298	Bemand et al., 1973	DF-RF/MS (a)
$(1.6 \pm 0.4) \times 10^{-13}$	298	Colussi, 1990	PLP-RF (b)
See Comment	248-312	Colussi et al., 1992	PLP-RF (c)
$2.4 \times 10^{-12} \exp[-(960 \pm 120)/T]$	243-400	Gleason et al., 1994	DF-RF (d)
$(1.0 \pm 0.3) \times 10^{-13}$	298		

Comments

- Discharge flow system. Two independent methods were used: $\text{O}(^3\text{P})$ atom decay in excess OCIO monitored by resonance fluorescence, and OCIO decay in excess $\text{O}(^3\text{P})$ determined by MS. There was only fair agreement between the two methods.
- Pulsed laser photolysis of OCIO at 308 nm, with the $\text{O}(^3\text{P})$ atom decay being determined by resonance fluorescence. The results were extrapolated to zero laser pulse intensity. Measurements were made over the pressure range 13 mbar to 1040 mbar of Ar. The observed rate coefficients were pressure dependent, indicating the presence of a termolecular association reaction. The value reported for the bimolecular component was not directly measured but was derived from fitting a falloff curve to the experimental data over the entire pressure range.
- Pulsed laser photolysis of OCIO at 308 nm, with the $\text{O}(^3\text{P})$ atom decay being determined by resonance fluorescence. The observed rate coefficients were pressure dependent, indicating the presence of a termolecular association reaction. A negative temperature dependence was observed for the bimolecular component, with the reported values of k increasing from $1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 312 K to $4.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 248 K. These values for the bimolecular component were not directly measured but were derived quantities which are consistent with falloff curves fitted to the experimental data over the pressure range 26 mbar to 800 mbar of Ar.
- Discharge flow system with resonance fluorescence detection of $\text{O}(^3\text{P})$ atoms. The total pressure was 1 mbar to 7 mbar. Measurements were made over the temperature range 200 K to 400 K. The data for the temperature range 243 K to 400 K were fitted with the Arrhenius expression given in the table. Data at lower temperatures showed a negative temperature dependence.

Preferred Values

$k = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.4 \times 10^{-12} \exp(-960/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240 K to 400 K.

Reliability

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

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are based on the results of the discharge flow-resonance fluorescence study of Gleason et al. (1994). Over the temperature range of the recommendation (240 K to 400 K), their data (Gleason et al., 1994) were well fit by the Arrhenius expression given, but at lower temperatures down to 200 K there was an abrupt change to a negative temperature dependence (Gleason et al., 1994). It appears that the experiments of Bemand et al. (1973) were complicated by secondary chemistry. The experiments of Colussi (1990) and Colussi et al. (1992) over an extended pressure range demonstrate the importance of the termolecular reaction (see separate data sheet on O + OClO + M). However, the extrapolated low pressure rate coefficients of Colussi (1990) and Colussi et al. (1992) show a negative temperature dependence over the range 248 K to 312 K, in contrast to the data of Gleason et al. (1994). Mauldin et al. (1997) have studied the mechanism and products of this system at 260 K and a total pressure of 430 mbar of N₂. Under these conditions the value of the rate coefficient for the reaction O + OClO → products was reported to be $1.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Mauldin et al. 1997). Combining this overall rate coefficient with the observation that the yield of ClO radicals under these conditions is <5% (Mauldin et al. 1997), leads to an upper limit of $k(\text{O} + \text{OClO} \rightarrow \text{O}_2 + \text{ClO}) < 1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 260 K. This upper limit to the rate coefficient is consistent with the value of Gleason et al. (1994), but not with the extrapolated values of Colussi et al. (1992).

References

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