# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iIOx15



This data sheet updated: 3rd February 2004.

$$IO + ClO \rightarrow ICl + O_2 \quad (1)$$
$$\rightarrow Cl + I + O_2 \quad (2)$$
$$\rightarrow Cl + OIO \quad (3)$$
$$\rightarrow I + OClO \quad (4)$$
$$IO + ClO + M \rightarrow IOOCl + M \quad (5)$$

$\Delta H°(1) = -200$ kJ·mol$^{-1}$
$\Delta H°(2) = 10$ kJ·mol$^{-1}$
$\Delta H°(3) = -19$ kJ·mol$^{-1}$
$\Delta H°(4) = -15$ kJ·mol$^{-1}$

### Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

| k/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(1.1 \pm 0.2) \times 10^{-11}$ | 298 | Bedjanian, Le Bras, and Poulet, 1997[1] | DF-MS (a) |
| $5.1 \times 10^{-12} \exp[(280 \pm 80)/T]$ | 200-362 | Turnipseed *et al*., 1997[2] | (b) |
| $(1.29 \pm 0.27) \times 10^{-11}$ | 298 | | |
| *Branching Ratios* | | | |
| $k_1/k = 0.20 \pm 0.02$ | 298 | Bedjanian, Le Bras, and Poulet, 1997[1] | (c) |
| $k_2/k = 0.25 \pm 0.02$ | 298 | | |
| $k_4/k = 0.55 \pm 0.03$ | 298 | | |
| $(k_1 + k_3)/k = 0.14 \pm 0.04$ | 298 | Turnipseed *et al*., 1997[2] | (d) |

### Comments

(a) The rate coefficient $k$ was determined from the decay of IO radicals in the presence of excess ClO under pseudo-first order conditions. The total pressure was 1.3 mbar He. $k$ was measured in four different reaction mixtures using $CF_3I$ and $I_2$ as sources of IO radicals, and OClO and $Cl_2O$ as sources of ClO radicals.

(b) Coupled DF-PLP system with LIF detection of IO radicals. IO radicals were photolytically generated in excess ClO, which was measured by UV absorption. The temporal profile of IO allowed accurate determination of $k$. I atoms were a major product, with a yield of $0.8 \pm 0.2$ at 298 K. Total pressure was 6.6 mbar to 21 mbar of $N_2$-He. The quoted errors include estimates of systematic errors.

(c) Quantitative detection of reaction products OClO, Cl and ICl, using both absolute and relative rate approaches to determine the branching ratios. The errors quoted are two least-squares standard deviations.

(d) Based on the ratio of the overall bimolecular rate coefficient determined from the first-order decay of IO in excess ClO (giving $k_1 + k_3$) with 4 x $10^{15}$ molecule $cm^{-3}$ of $O_3$ present, to the total rate coefficient $k$ determined in a similar manner with no excess $O_3$ present. At 223 K the yield of I atoms was 0.78 ± 0.25, suggesting that the I atom yield does not vary significantly with temperature over the range 223 K to 298 K.

## Preferred Values

$k = 1.2 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K.
$k = 4.7 \times 10^{-12} \exp(280/T)$ $cm^3$ $molecule^{-1}$ $s^{-1}$ over the temperature range 200 K to 370 K.
$k_1/k = 0.20$ at 298 K.
$k_2/k = 0.25$ at 298 K.
$k_4/k = 0.55$ at 298 K.

*Reliability*

$\Delta\log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.
$\Delta(k_1/k) = 0.10$ at 298 K.
$\Delta(k_2/k) = 0.10$ at 298 K.
$\Delta(k_4/k) = 0.10$ at 298 K.

*Comments on Preferred Values*

The two experimental studies of Bedjanian *et al.*[1] and Turnipseed *et al.*,[2] which used different techniques, give overall rate coefficients $k$ which are in excellent agreement at 298 K. The recommended value is a simple mean of the two results.[1,2] The temperature dependence from Turnipseed *et al.*[2] is consistent with those observed for other exothermic XO + YO reactions and is accepted for the recommendation.

The quantitative information from the two studies[1,2] concerning the product channels is consistent within the cited uncertainties, with the discharge flow study of Bedjanian *et al.*[1] giving more detailed data and being used for the recommendation. The overall rate coefficient is accounted for by reactions (1) + (2) + (4) and it is concluded that reaction (3) is negligible. Provisionally, the branching ratios at 298 K can be applied to stratospheric temperatures since the I atom yield exhibits no significant temperature dependence.[2]

## References


1 Y. Bedjanian, G. Le Bras, and G. Poulet, J. Phys. Chem. A **101**, 4088 (1997).
2 A. A. Turnipseed, M. K. Gilles, J. B. Burkholder, and A. R. Ravishankara, J. Phys. Chem. A **101**, 5517 (1997).