# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx41



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## $OClO + NO_3 \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $< 1 \times 10^{-15}$ | 300 | Biggs *et al*., 1991[1] | DF-UV |
| $2 \times 10^{-14}$ | 298 | Friedl, Sander, and Yung, 1992[2] | (a) |
| $2 \times 10^{-14}$ | 220 | | |
| $< 6 \times 10^{-17}$ | 298-300 | Boyd, Marston, and Wayne, 1996[3] | (b) |

### Comments

(a) The experiments were carried out in a long-path absorption flow reactor. $NO_3$ radicals were generated by the reaction of F atoms with $HNO_3$ or of Cl atoms with $ClONO_2$. The products were analysed by IR and UV absorption measurements. Rate constant at 298 K derived by computer simulation of $NO_3$, OClO and ClO profiles, and assuming $NO_2 + O_2 + ClO$ are products. At 220 K and 5.3 mbar He, formation of chlorylnitrate ($O_2ClONO_2$) in a termolecular reaction channel was observed, with an apparent rate constant of $2 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. At this temperature the rate constant for the bimolecular channel was derived to be $2 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

(b) Room temperature studies at low pressure in discharge stopped flow (typically 10.7 mbar), slow flow (typically 8 mbar) and discharge flow (2.7 mbar) experiments. Detection of both $NO_3$ and OClO was achieved using absorption spectroscopy. The slow flow experiments are comparable to those of Friedl *et al*.[2]

### Preferred Values

No recommendation is given.

*Comments on Preferred Values*

The available results of the studies of this reaction are very divergent. In their later study, Boyd *et al*.[3] were unable to interpret their observations, obtained in three different set ups, in terms of a gas-phase reaction between $NO_3$ and OClO, and suggest that heterogeneous processes play an important role in their study, and potentially therefore also in the similar study of Friedl *et al*.[2] Further work is clearly needed to resolve these discrepancies, and until this is available no recommendation is given, other than to note that the reaction is slow.

## References


[1] P. Biggs, M. H. Harwood, A. D. Parr and R. P. Wayne, J. Phys. Chem. **95**, 7746 (1991).
[2] R. R. Friedl, S. P. Sander, and Y. L. Yung, J. Phys. Chem. **96**, 7490 (1992).
[3] A. A. Boyd, G. Marston and R. P. Wayne, J. Phys. Chem. **100**, 130 (1996).