# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx8



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## Br + OClO → BrO + ClO

$\Delta H° = 15$ kJ·mol$^{-1}$

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $4.2 \times 10^{-13}$ | 298 | Clyne and Watson, 1977[1] | DF-MS (a) |
| $2.5 \times 10^{-11} \exp(-1336/T)$ | 267-423 | Toohey, 1988[2] | DF-RF (b) |
| $(2.82 \pm 0.03) \times 10^{-13}$ | 299 | | |

### Comments

(a) MS detection of OClO in an excess of Br atoms. The observed decays were first-order, but computer modeling was used to correct for the effects of the reverse reaction.

(b) The measured rate coeficients (in cm$^3$ molecule$^{-1}$ s$^{-1}$ units) were: 267 K, $(1.70 \pm 0.03) \times 10^{-13}$; 294 K, $(2.63 \pm 0.04) \times 10^{-13}$; 299 K, $(2.82 \pm 0.03) \times 10^{-13}$; 325 K, $(4.03 \pm 0.07) \times 10^{-13}$; 351 K, $(5.45 \pm 0.22) \times 10^{-13}$; 385 K, $(7.88 \pm 0.24) \times 10^{-13}$; and 423 K, $(1.06 \pm 0.04) \times 10^{-12}$. A unit-weighted least-squares fit of these data to the Arrhenius expression results in $k = 2.5 \times 10^{-11} \exp(-1336/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over the temperature range 267 K to 423 K.

### Preferred Values

$k = 3.5 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K.

$k = 2.7 \times 10^{-11} \exp(-1300/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over the temperature range 260 K to 430 K.

*Reliability*

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

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

*Comments on Preferred Values*

The preferred value at 298 K is the mean of the values reported by Clyne and Watson[1] and Toohey.[2] In the former study[1] corrections were made for the effects of the reverse reaction, which was not done in the earlier study by Clyne and Coxon[3] and which is therefore not used in this evaluation. The temperature dependence of $k$ obtained by Toohey[2] is accepted, but with substantial uncertainty limits in the absence of confirmatory studies, and is combined with the preferred value of $k$ at 298 K to obtain the preferred Arrhenius expression.

## References


[1] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **73**, 1169 (1977).

[2] D. W. Toohey, "Kinetic and Mechanistic Studies of Reactions of Bromine and Chlorine Species Important in the Earth's Stratosphere", Ph.D. Thesis, Harvard University, Cambridge, MA (1988).

[3] M. A. A. Clyne and J. A. Coxon, Proc. Roy. Soc. London **A298**, 424 (1967).