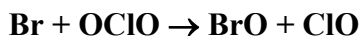


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx8

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be re-transmitted or disseminated either electronically or in hard copy without explicit written permission.

This data sheet updated: 25<sup>th</sup> September 2003.



$$\Delta H^\circ = 15 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

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

### Comments

- (a) MS detection of OCIO 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 coefficients (in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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  $k = 2.5 \times 10^{-11} \exp(-1336/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 267 K to 423 K.

### Preferred Values

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

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

### Reliability

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

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

### Comments on Preferred Values

The preferred value at 298 K is the mean of the values reported by Clyne and Watson<sup>1</sup> and Toohey.<sup>2</sup> In the former study<sup>1</sup> corrections were made for the effects of the reverse reaction, which was not done in the earlier study by Clyne and Coxon<sup>3</sup> and which is therefore not used in this evaluation. The temperature dependence of  $k$  obtained by Toohey<sup>2</sup> 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

- <sup>1</sup> M. A. A. Clyne and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **73**, 1169 (1977).
- <sup>2</sup> 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).
- <sup>3</sup> M. A. A. Clyne and J. A. Coxon, *Proc. Roy. Soc. London* **A298**, 424 (1967).