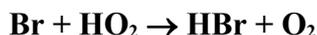


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx4

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



$$\Delta H^\circ = -162.8 \text{ kJ}\cdot\text{mol}^{-1}$$

## Rate coefficient data

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference                                     | Technique/ Comments |
|--|---------|---|---------------------|
| <i>Absolute Rate Coefficients</i>                    |         |   |                     |
| $1.4 \times 10^{-11} \exp[-(590 \pm 140)/T]$         | 260-390 | Toohey, Brune and Anderson, 1987 <sup>1</sup> | DF-LMR/RF (a)       |
| $(2.0 \pm 0.3) \times 10^{-12}$                      | 298     |   |                     |
| $(1.5 \pm 0.2) \times 10^{-12}$                      | 298     | Laverdet <i>et al.</i> , 1990 <sup>2</sup>    | DF-EPR (b)          |
| $4.9 \times 10^{-12} \exp[-(310 \pm 40)/T]$          | 230-355 | Bedjanian <i>et al.</i> , 2001 <sup>3</sup>   | DF-MS (c)           |
| $(1.71 \pm 0.20) \times 10^{-12}$                    | 297     |   |                     |

## Comments

- (a) Br atoms generated either directly by discharge of Br<sub>2</sub>, or from the addition of diluted Br<sub>2</sub> to an excess of O(<sup>3</sup>P) atoms. HO<sub>2</sub> radicals were generated by the F + H<sub>2</sub>O<sub>2</sub> reaction. HO<sub>2</sub> radicals and Br atoms were monitored by laser magnetic resonance and resonance fluorescence, respectively. *k* was determined from pseudo-first order decay of HO<sub>2</sub> in the presence of excess Br.
- (b) Br atoms generated either directly by discharge of Br<sub>2</sub>, or from the Cl + CH<sub>2</sub>=CHBr reaction. HO<sub>2</sub> radicals were generated from the reaction of Cl with CH<sub>3</sub>OH in the presence of O<sub>2</sub>. *k* was determined from pseudo-first order decay of HO<sub>2</sub> in the presence of excess Br. A reinterpretation of previous indirect measurements conducted in the same laboratory (Poulet *et al.*<sup>4</sup>) is also given. This yielded revised values of *k* in the range  $(1.0\text{-}2.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (c) Br atoms generated either directly by discharge of Br<sub>2</sub>, or from the H + Br<sub>2</sub> or Cl + Br<sub>2</sub> reactions. HO<sub>2</sub> radicals were generated by the F + H<sub>2</sub>O<sub>2</sub> reaction. *k* was determined from pseudo-first order decay of HO<sub>2</sub> in the presence of excess Br.

## Preferred Values

$k = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 7.7 \times 10^{-12} \exp(-450/T) \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230 K to 390 K.

### Reliability

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta(E/R) = \pm 200$  K.

### Comments on Preferred Values

The preferred value at 298K is the mean of the results of Toohey *et al.*,<sup>1</sup> Laverdet *et al.*<sup>2</sup> and Bedjanian *et al.*,<sup>3</sup> which are all in acceptable agreement. The preferred Arrhenius expression is based on the mean of the  $E/R$  values from the temperature dependence studies of Toohey *et al.*<sup>1</sup> and Bedjanian *et al.*,<sup>3</sup> combined with a pre-exponential factor adjusted to give the preferred value of  $k$  at 298 K. The uncertainty in the preferred value of  $E/R$  reflects the fact that the values reported by Toohey *et al.*<sup>1</sup> and Bedjanian *et al.*<sup>3</sup> differ by almost a factor of two. The observed kinetics are consistent with the mechanism proceeding via direct hydrogen atom abstraction to yield HBr, as also indicated by theoretical studies of the reaction.<sup>5</sup>

### References

- <sup>1</sup> D. W. Toohey, Wm. H. Brune, and J. G. Anderson, *J. Phys. Chem.* **91**, 1215 (1987).
- <sup>2</sup> G. Laverdet, G. Le Bras, A. Mellouki, and G. Poulet, *Chem. Phys. Lett.* **172**, 430 (1990).
- <sup>3</sup> Y. Bedjanian, V. Riffault, G. Le Bras and G. Poulet, *J. Phys. Chem. A* **105**, 573 (2001).
- <sup>4</sup> G. Poulet, G. Laverdet, and G. Le Bras, *J. Chem. Phys.* **80**, 1922 (1984).
- <sup>5</sup> R. Sumathi and S. D. Peyerimhoff, *Phys. Chem. Chem. Phys.* **1**, 3973 (1999).