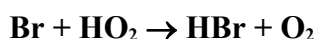


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx4

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: 25th 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 ¹	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 ²	DF-EPR (b)
$4.9 \times 10^{-12} \exp[-(310 \pm 40)/T]$	230-355	Bedjanian <i>et al.</i> , 2001 ³	DF-MS (c)
$(1.71 \pm 0.20) \times 10^{-12}$	297		

Comments

- (a) Br atoms generated either directly by discharge of Br₂, or from the addition of diluted Br₂ to an excess of O(³P) atoms. HO₂ radicals were generated by the F + H₂O₂ reaction. HO₂ radicals and Br atoms were monitored by laser magnetic resonance and resonance fluorescence, respectively. *k* was determined from pseudo-first order decay of HO₂ in the presence of excess Br.
- (b) Br atoms generated either directly by discharge of Br₂, or from the Cl + CH₂=CHBr reaction. HO₂ radicals were generated from the reaction of Cl with CH₃OH in the presence of O₂. *k* was determined from pseudo-first order decay of HO₂ in the presence of excess Br. A reinterpretation of previous indirect measurements conducted in the same laboratory (Poulet *et al.*⁴) 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 Br₂, or from the H + Br₂ or Cl + Br₂ reactions. HO₂ radicals were generated by the F + H₂O₂ reaction. *k* was determined from pseudo-first order decay of HO₂ 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.*,¹ Laverdet *et al.*² and Bedjanian *et al.*,³ 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.*¹ and Bedjanian *et al.*,³ 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.*¹ and Bedjanian *et al.*³ 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.⁵

References

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