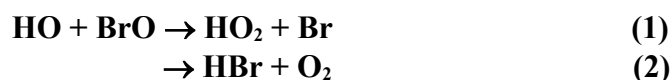


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx13

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.



$$\Delta H^\circ(1) = -30 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -193 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(7.5 \pm 4.2) \times 10^{-11}$	300	Bogan <i>et al.</i> , 1996 <sup>1</sup>	DF-MS (a)
$(4.5 \pm 1.8) \times 10^{-11}$	298	Gilles <i>et al.</i> , 2001 <sup>2</sup>	DF (b)
$1.65 \times 10^{-11} \exp[(250 \pm 50)/T]$	230-355	Bedjanian <i>et al.</i> 2001 <sup>3</sup>	DF-MS (c)
$(3.6 \pm 0.9) \times 10^{-11}$	300		(d)
$(3.9 \pm 1.0) \times 10^{-11}$	298		(e)
$(3.85 \pm 0.70) \times 10^{-11}$	299		(f)
<i>Branching ratios</i>			
$k_2/k \leq 0.03$	298	Bedjanian <i>et al.</i> 2001 <sup>3</sup>	DF-MS (g)

### Comments

- (a) BrO radicals generated by passing a O<sub>2</sub>-Br<sub>2</sub>-He mixture through a microwave discharge. HO radicals generated by the reaction of F atoms (generated in a second microwave discharge) with H<sub>2</sub>O. BrO radical concentrations were obtained by titration with NO and measurement of the resulting NO<sub>2</sub> by MS. HO radical concentrations were obtained by titration with Br<sub>2</sub> and measurement of the depletion of Br<sub>2</sub> by MS. The rate coefficient was derived from modelling using a chemical mechanism involving 18 reactions.
- (b) BrO radicals generated from Br + O<sub>3</sub> reaction (following discharge of Br<sub>2</sub>). HO radicals generated from pulsed 248 nm laser photolysis of O<sub>3</sub> in the presence of H<sub>2</sub>O. BrO and HO were measured by UV absorption and LIF, respectively. Experiments carried out under pseudo-first order conditions with HO in excess.
- (c) BrO generated from either from O(<sup>3</sup>P) + Br<sub>2</sub> (following discharge of O<sub>2</sub>), or from Br + O<sub>3</sub> (following discharge of Br<sub>2</sub>). Br was also generated by F + HBr (following discharge of F<sub>2</sub>) for mechanistic studies. HO was generated from either H + NO<sub>2</sub> (following discharge of H<sub>2</sub> or F + H<sub>2</sub>), or F + H<sub>2</sub>O (following discharge of F<sub>2</sub>). BrO and HO concentrations were measured directly at their parent peaks. Experiments carried out under pseudo-first order conditions with HO in excess.  $k$  also determined relative to  $k(\text{HO} + \text{Br}_2)$  in a separate series of experiments. Results of the two methods are in good agreement and the reported rate coefficient is based on the combined dataset.

- (d) HO generated by H + NO<sub>2</sub>.
- (e) HO generated by F + H<sub>2</sub>O.
- (f) Relative rate measurement.
- (g) Based on detection of HBr.

### Preferred Values

$k = 4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.8 \times 10^{-11} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230 K to 350 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 298K is based on the room temperature data of Gilles *et al.*<sup>2</sup> and Bedjanian *et al.*<sup>3</sup> The previous study of Bogan *et al.*<sup>1</sup> is also consistent with this recommendation. The preferred Arrhenius expression is based on the  $E/R$  value from the temperature dependence study of Bedjanian *et al.*,<sup>3</sup> combined with a pre-exponential factor adjusted to give the preferred value of  $k$  at 298 K. The results of Bedjanian *et al.*<sup>3</sup> are consistent with channel (a) being the dominant, if not sole, pathway. This conclusion is supported by the theoretical study of Sumathi and Peyerimhoff.<sup>4</sup>

### References

- <sup>1</sup> D. J. Bogan, R. P. Thorn, F. L. Nesbitt, and L. J. Stief, *J. Phys. Chem.* **100**, 14383 (1996).
- <sup>2</sup> M. K. Gilles, D. C. McCabe, J. B. Burkholder and A. R. Ravishankara, *J. Phys. Chem. A* **105**, 5849 (2001).
- <sup>3</sup> Y. Bedjanian, V. Riffault, G. Le Bras and G. Poulet, *J. Phys. Chem. A* **105**, 6154 (2001).
- <sup>4</sup> R. Sumathi and S. D. Peyerimhoff. *Phys. Chem. Chem. Phys.* **1**, 3973 (1999).