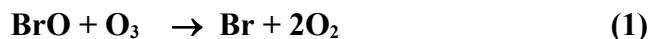


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx18

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.



$$\Delta H^\circ(1) = -151 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -99 \text{ kJ}\cdot\text{mol}^{-1}$$

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>			
$\sim 10^{-17}$	318-343	Rattigan, et al., 1995	P-AS (a)
$k_2 = 7 \times 10^{-14} \exp[-(3100 \pm 350)/T]$	318-343		
$k_2 = 2.1 \times 10^{-18}$	298*		
$< (2.1 \pm 0.7) \times 10^{-17}$	298	Rowley et al., 1996	FP-AS (b)
$k_2 = (1.66 \pm 0.11) \times 10^{-18}$	298		

Comments

- (a) Photolysis of Br₂-O₃ mixtures at 380 nm to 480 nm in N₂ or O₂ bath gas at total pressures in the range 16 mbar to 1000 mbar. Time-resolved UV absorption spectroscopy was used to monitor the concentrations of O₃, Br₂ and BrO radicals before, during, and after irradiation. OBrO was also detected in absorption in the wavelength range 400 nm to 600 nm.
- (b) Flash photolysis-long-path UV absorption technique. BrO radicals were produced by photolysis at ~400 nm of Br₂ in an excess of O₃. Time-resolved UV/visible absorption spectra of BrO were recorded over the range 234 nm to 367 nm and of OBrO over the range 425 nm to 558 nm. The BrO decay was largely due to the BrO + BrO reaction but deviations from second-order behavior were observed at high O₃ concentrations, and attributed to the BrO + O₃ reaction. The upper limit was derived from an analysis of the [BrO] temporal profiles at high O₃ concentrations.

Preferred Values

$$k < 2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The two most recent studies of Rattigan et al. (1995) and Rowley et al. (1996) are in good agreement and set a lower upper limit to the rate coefficient for this reaction than did previous studies (Sander and Watson, 1981; Mauldin III et al., 1993). The preferred upper limit to k at 298 K is therefore based on the results reported by Rattigan et al. (1995) and Rowley et al. (1996). Previously, the reaction of BrO with O₃ had been assumed to occur exclusively by

channel (1), but the positive identification of OBrO as a reaction product indicates that channel (2) is likely to be significant. The existing determinations of k_2 are in good agreement (Rattigan et al., 1995; Rowley et al., 1996) but involve significant uncertainties. Further studies are necessary before a branching ratio can be recommended.

References

- Mauldin III, R. L., Wahner, A. and Ravishankara, A. R.: J. Phys. Chem. 97, 7585, 1993.
Rattigan, O. V., Cox, R. A. and Jones, R. L.: J. Chem. Soc. Faraday Trans. 91, 4189, 1995.
Rowley, D. M., Harwood, M. H., Freshwater, R. A. and Jones, R. L.: J. Phys. Chem. 100, 3020, 1996.
Sander, S. P. and Watson, R. T.: J. Phys. Chem. 85, 4000, 1981.