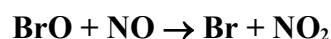


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx19

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: 23th July 2003.



$$\Delta H^\circ = -65 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(2.2 \pm 0.4) \times 10^{-11}$	298	Clyne and Watson, 1975 ¹	DF-MS (a)
$7.11 \times 10^{-12} \exp[(296 \pm 10)/T]$	230-425	Leu, 1979 ²	DF-MS (a)
$(1.89 \pm 0.16) \times 10^{-11}$	298		
$1.28 \times 10^{-11} \exp[(181 \pm 46)/T]$	224-398	Watson, Sander, and Yung, 1979 ³	FP-UVA (b)
$(2.15 \pm 0.25) \times 10^{-11}$	298		
$(2.15 \pm 0.18) \times 10^{-11}$	298	Ray and Watson, 1981 ⁴	DF-MS (a)

Comments

- (a) BrO radicals were produced by the O + Br₂ reaction and monitored by MS in an excess of NO.
- (b) BrO radicals were produced by the flash photolysis of Br₂-O₂ mixtures in the presence of an excess of NO. BrO radical concentrations were monitored by UV absorption at 339 nm. *k* was observed to be independent of pressure over the range 130 mbar to 930 mbar of He or N₂.

Preferred Values

$$k = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 8.7 \times 10^{-12} \exp(260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220 \text{ K to } 430 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

The results of the three low pressure mass spectrometric studies of Clyne and Watson,¹ Leu² and Ray and Watson⁴ and the high pressure UV absorption study of Watson *et al.*,³ all of which used pseudo-first order conditions, are in excellent agreement at 298 K and are considered to be more reliable than the earlier low pressure UV absorption study of Clyne and Cruse.⁵ The results of the two temperature dependence studies^{2,3} are in good agreement. The preferred Arrhenius expression is derived from a least-squares fit to all the data of Clyne and Watson,¹ Leu,² Watson *et al.*³ and Ray and Watson.⁴ By combining the data reported in the

high pressure UV absorption study³ with those from the mass spectrometric studies,^{1,2,4} this reaction does not exhibit any observable pressure dependence between 1 mbar and 1 bar total pressure. The temperature dependencies of the rate coefficients for the analogous ClO and HO₂ reactions are also negative and similar in magnitude.

References

- ¹ M. A. A. Clyne and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **71**, 336 (1975).
- ² M.-T. Leu, *Chem. Phys. Lett.* **61**, 275 (1979).
- ³ R. T. Watson, S. P. Sander, and Y. L. Yung, *J. Phys. Chem.* **83**, 2936 (1979).
- ⁴ G. W. Ray and R. T. Watson, *J. Phys. Chem.* **85**, 2955 (1981).
- ⁵ M. A. A. Clyne and H. W. Cruse, *Trans. Faraday Soc.* **66**, 2227 (1970).