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

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$BrO + NO \rightarrow Br + NO_2$

$\Delta H° = -65$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.4) \times 10^{-11}$	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 + Br_2 reaction and monitored by MS in an excess of NO.

(b) BrO radicals were produced by the flash photolysis of Br_2-O_2 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 N_2.

Preferred Values

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

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

Reliability

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

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

Comments on Preferred Values

The results of the three low pressure mass spectrometric studies of Clyne and Watson,[1] Leu[2] and Ray and Watson[4] 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 study[3] 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 HO_2 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).