IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC29

This data sheet updated: 12th November 2002.

$Br + C_2H_2 + M \rightarrow BrC_2H_2 + M$
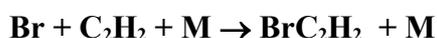
Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(4.0 ± 0.8) x 10^{-15}	210-393	Payne *et al*., 1986[1]	FP-RF (a)
Relative Rate Coefficients			
(4.5 ± 0.9) x 10^{-15}	295	Wallington *et al*., 1989[2]	RR (b)
(3.90 ± 0.16) x 10^{-14} (1013 mbar air)	298	Barnes *et al*., 1989[3]	RR (c)
(4.93 ± 0.20) x10^{-14} (1013 mbar air)	298		RR (d)
(3.51 ± 0.18) x10^{-14} (1013 mbar air)	313		
(2.44 ± 0.10) x10^{-14} (1013 mbar air)	333		
(1.78 ± 0.06) x10^{-14} (1013 mbar air)	353		
(3.94 ± 0.28) x10^{-14} (940 mbar air)	239	Ramacher, Orlando and Tyndall, 2001[4]	RR (e)
(3.59 ± 0.25) x10^{-14} (940 mbar air)	249		
(3.72 ± 0.26) x10^{-14} (940 mbar air)	261		
(3.24 ± 0.23) x10^{-14} (940 mbar air)	280		
(2.55 ± 0.18) x10^{-14} (940 mbar air)	296		

Comments

(a) Flash photolysis of CH$_3$Br ($\lambda > 195$ nm) as Br source. Rate coefficient was independent of pressure between 20 and 133 mbar Ar.

(b) CW photolysis of Br$_2$ in the presence of C$_2$H$_2$ in 986 mbar (740 Torr) N$_2$ and 2-methylpropane as reference reactant. Depletion of reactants followed by GC to derive k(Br + C$_2$H$_2$) / k(Br + 2-methylpropane) = 2.96 $\pm$ 0.11. The rate coefficient was placed on an absolute basis using k(Br + 2-methylpropane) = 1.52x10^{-15} cm^3 molecule^{-1} s^{-1} at 295 K.[5]

(c) CW photolysis of Br$_2$ (300 – 500 nm) in the presence of C$_2$H$_2$ in 33 – 1013 mbar (25 – 760 Torr) N$_2$/O$_2$ bath gas and CH$_3$CHO as reference reactant. At 298 K and a total pressure of 760 Torr air, k(Br + C$_2$H$_2$) / k(Br + CH$_3$CHO) = (1.0 $\pm$ 0.04) x10^{-2}. Rate coefficient put on an absolute basis using k(Br + CH$_3$CHO) = 3.9 x10^{-12} cm^3 molecule^{-1} s^{-1}. [6]

(d) As (c) but using 2,2,4-trimethylpentane (TMP) as reference compound. Data put on absolute basis using k(Br + TMP) = (4.16 $\pm$ 0.33)x10^{-12} (exp-1820/T),[3] which itself was measured relative to k(Br + 2-methylpropane) = 1.83x10^{-10} exp (-3452/T).[5]

(e) Photolysis of Br$_2$ ($\lambda > 420$ nm) in presence of C$_2$H$_2$ in 933- 946 mbar (700 – 710 Torr) air, and C$_2$H$_4$ as reference reactant. Depletion of reactants followed by FTIR absorption spectroscopy. k(Br + C$_2$H$_2$) / k(Br + C$_2$H$_4$) = (6.9 $\pm$ 0.5)x10^{-2} at 239 K, (7.9 $\pm$ 0.5)x10^{-2} at 249 K, (9.6 $\pm$ 0.7) x10^{-2} at 261 K, (13.5 $\pm$ 0.9) x10^{-2} at 280 K and (19.3 $\pm$ 1.4) x10^{-2} at 296 K. Rate coefficients put on an absolute basis using k(Br + C$_2$H$_4$) = 5.71, 4.54, 3.87, 2.40 and 1.32x10^{-13} cm^3 molecule^{-1} s^{-1} at 239 K, 249 K, 261 K, 280 K and 296 K, respectively (see Br

+ C_2H_4 data sheet). The reference value for k(Br + C_2H_4) at 261 K is the average of the values obtained using HCHO and CH_3CHO as reference reactants.

Preferred Values

$k = 2.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 296 K and 1 bar air.

$k(T) = 6.35 \times 10^{-15}$ exp (440/T) (for air as bath gas, and pressures close to 1 bar) over the temperature range 230 K to 300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 200$

Comments on Preferred Values

The measured rate coefficients reveal a strong dependence on total pressure,[3] temperature[3,4] and the O_2 partial pressure.[3] This has been taken to indicate[3] that the mechanism involves formation of a Br-C_2H_2 adduct, which can dissociate to reactants or react with O_2 to form a peroxy radical. For this reason, the effective rate coefficient is significantly higher in air than in an oxygen free bath gas at total pressures of up to an atmosphere. There is insufficient data to describe the temperature, pressure and [O_2] dependencies of the rate coefficient, and our recommendation is restricted to air as bath gas, and pressures close to 1 bar. The data presented by Ramacher *et al.*[4] using C_2H_4 as reference reactant is preferred over measurements relative to 2,2,4-trimethylpentane for reasons discussed by these authors, and form the basis of our recommendation. The temperature dependence of the rate coefficient was derived by least squares fitting of the data listed. Further studies of the rate coefficient in air at low pressures and temperatures would be useful to aid modelling of the role of this reaction at high altitudes.

The formation of stable products when the reaction is initiated in air (in absence of NO*x*) appears to be independent of temperature[4] and involves bimolecular reactions of the initially formed CHBr=CH radical with O_2 to form CO, HC(O)OH, HC(O)Br and CO_2 (see references 3,4 and 7 for details).

References

[1] W.A. Payne, D.F. Nava, J. Brunning and L.J. Stief, J. Geophys. Res. **91**, 4097 (1986).

[2] T.J. Wallington, L.M. Skewes, W.O. Siegl, S.M. Japar, Int. J. Chem. Kin. **21**, 1069 (1989).

[3] I. Barnes, V. Bastian, K.H. Becker, R. Overath, Z. Tong, Int. J. Chem. Kin. **21**, 499 (1989).

[4] B. Ramacher, J.J. Orlando, G.S. Tyndall, Int. J. Chem. Kin. **33**, 198 (2001).

[5] J.J. Russell, J.A. Seetula, R.S. Timonen, D. Gutman and D.F. Nava, J. Am. Chem. Soc. **110**, 3084 (1988).

[6] IUPAC (2012), http://iupac.pole-ether.fr

[7] G. Yarwood, N. Peng and H. Niki, J. Phys. Chem. **95**, 7330 (1991).