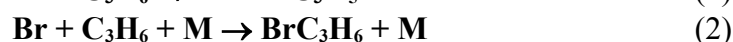


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC31

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This data sheet updated: 12th November 2002.



$$\Delta\text{Hr}(1) = 2.9 \text{ kJ} \cdot \text{mol}^{-1} \text{ (reference 2)}$$

$$\Delta\text{Hr}(2) = -32.2 \text{ kJ} \cdot \text{mol}^{-1} \text{ (reference 2)}$$

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>			
$k_1 = 8.3 \times 10^{-12} \exp[-(2200 \pm 300)/T]$	263 - 363	Kondo, Marshall and Benson, F-MS (a) 1988 ¹	
$k_1 = 8.15 \times 10^{-13} \exp[-(1250 \pm 160)/T]$	233 - 320	Bedjanian, Poulet and Le Bras, DF-MS (b) 1998 ²	
$k_1 = 1.2 \times 10^{-14}$	298		
$k_2 = 3.8 \times 10^{-33} \exp[(1200 \pm 50)/T] [\text{He}]$	233 - 320		
<i>Relative Rate Coefficients</i>			
$k = (4.2 \pm 0.5) \times 10^{-12}$	295	Wallington <i>et al.</i> , 1989 ³	RR (c)
$k = (2.9 \pm 0.3) \times 10^{-12}$	298	Barnes <i>et al.</i> , 1989 ⁴	RR (d)

Comments

- (a) Very low pressure reactor at $\approx 1 \times 10^{-3}$ mbar with bromine atoms detected directly using a mass spectrometer. The Arrhenius expression was derived from a calculated pre-exponential factor associated with a bent transition state, combined with the most reliable rate coefficient, which was that obtained at 363 K.
- (b) Experiments conducted at pressures of 0.7 – 2.7 mbar (0.5 – 2 Torr) He. Br was detected as BrCl after titration with NOCl. Consistent kinetic data for k_1 was derived by monitoring either Br, HBr or C₃H₅Br (formed in C₃H₅ + Br). For determination of k_2 , Br₂ was added to partly convert the BrC₃H₆ radical to BrC₃H₆Br, which could be detected, and to regenerate Br. Values of k_2 at pressures of 0.7 to 2.7 mbar (0.5 to 2 Torr) He and 233 to 308 K were then derived by fitting to an analytical expression assuming a steady state for Br. An approximately linear dependence on He pressure was observed indicating that the derived values of k_2 are close to the low-pressure limit.
- (c) CW photolysis of Br₂ in the presence of C₃H₆ in 986 mbar (740 Torr) air and CH₃CHO as reference reactant. The depletion of reactants was followed by GC to derive $k(\text{Br} + \text{C}_3\text{H}_6) / k(\text{Br} + \text{CH}_3\text{CHO}) = (1.10 \pm 0.12)$. An absolute rate coefficient was calculated using $k(\text{Br} + \text{CH}_3\text{CHO}) = 3.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K.⁵

- (d) CW photolysis of Br₂ (300 – 500 nm) in the presence of C₃H₆ in 1013 mbar (760 Torr) N₂/O₂ bath gas and CH₃CHO as reference compound. Depletion of reactants monitored by FTIR to derive $k(\text{Br} + \text{C}_3\text{H}_6) / k(\text{Br} + \text{CH}_3\text{CHO}) = (0.75 \pm 0.07)$. An absolute rate coefficient was calculated using $k(\text{Br} + \text{CH}_3\text{CHO}) = 3.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.⁵

Preferred Values

$k_1 = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K

$k_1 = 8.1 \times 10^{-13} \exp -(1250 / T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230 K to 320 K.

$k = 3.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K and 1 atmosphere air.

Reliability

$\Delta \log k_1 = \pm 0.2$ at 296 K.

$\Delta(E/R) = \pm 500 (k_1)$

$\Delta \log k = \pm 0.2$ at 298 K and one atmosphere air.

Comments on Preferred Values

The reaction proceeds via both direct abstraction (k_1) and via a termolecular channel (k_2) involving formation of a BrC₃H₆ adduct that can redissociate to products or react with O₂. The effective overall rate coefficient therefore displays a dependence on temperature, total pressure and the oxygen partial pressure.⁴ The study of Bedjanian *et al.*² is considered the more reliable measurement of k_1 as the work of Kondo *et al.*¹ may have been influenced by the presence of excited states of Br. The recommended value for k_1 is therefore based on the work of Bedjanian *et al.*¹, with expanded error limits.

In the absence of kinetic data for k_2 in the fall off regime it is not possible to derive a parameterisation of the rate coefficient for all atmospheric conditions. Instead, for the overall rate coefficient, we recommend an average of the results of the relative rate studies^{3,4} at 298 K and note that the branching ratio to k_1 (i.e. to HBr formation) under atmospheric conditions is given by k_1/k . Pressure and temperature dependent studies in the fall-off regime are needed to model this reaction at high altitudes in the atmosphere where the pressure and temperature are lower. The structure of the radical product of the abstraction channel (1) is believed to be CH₂=CHCH₂ indicating that abstraction from the CH₃ group is most important.¹

References

- ¹ O. Kondo, R.M. Marshall and S.W. Benson, *Int. J. Chem. Kin.*, **20**, 297 (1988).
- ² Y. Bedjanian, G. Poulet and G. Le Bras, *J. Phys. Chem. A.*, **102**, 5867 (1998).
- ³ T.J. Wallington, L.M. Skewes, W.O. Siegl, S.M. Japar, *Int. J. Chem. Kin.* **21**, 1069 (1989).
- ⁴ I. Barnes, V. Bastian, K.H. Becker, R. Overath, Z. Tong, *Int. J. Chem. Kin.* **21**, 499 (1989).
- ⁵ IUPAC (2013), <http://iupac.pole-ether.fr>