IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PBr10

This data sheet updated: 15th December 2000.

$CH_3Br + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CH_3Br + h\nu \rightarrow CH_3 + Br$	296	404

Absorption cross-section data

Wavelength range/nm	Reference	Comments
180-260	Gillotay and Simon, 1988 [1]	(a)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(Br) = 1.01 \pm 0.16$	248	Talukdar, Vaghjiani, and Ravishankara, 1992[2]	(b)
$\phi(Br) = 1.10 \pm 0.20$	222		
$\phi(Br) = 1.05 \pm 0.11$	193		
$\phi(H) = 0.002 \pm 0.001$	193		

Comments

(a) Spectra were obtained using a thermostatted absorption cell with a single pass optical path of 2 m coupled to a monochromator capable of a maximum resolution of 0.015 nm. Pressures of CH_3Br used covered the range 5.3 x 10^{-2} – 29 mbar. Spectra were recorded at 295 K, 270 K, 250 K, 230 K, and 210 K. The data were fitted to a polynomial expression giving the cross sections as a function of temperature and pressure.

(b) Pulsed laser photolysis of CH_3Br-N_2 or He mixtures and detection of $Br(^2P_{3/2})$ by resonance fluorescence. A small amount of H_2 was added to ensure rapid quenching of the $Br(^2P_{1/2})$ also produced. The $Br(^2P_{3/2})$ measurements were calibrated by HBr photolysis at 193 nm for which a quantum yield of unity was assumed. No H atom production could be detected in the 248 nm and 222 nm photolyses.

Preferred Values

Absorption cross-sections of CH_3Br at 295 K and 209 K.

λ/nm	10^{20} σ/cm^2		λ/nm	10^{20} σ/cm^2	
	295 K	210 K		295 K	210 K
190	43.9	(a)	226	23.0	21.6
192	52.9	(a)	228	18.8	17.7
194	62.0	(a)	230	15.4	14.4
196	69.1	(a)	232	12.4	11.4
198	76.0	(a)	234	9.87	8.86
200	79.1	(a)	236	7.65	6.58
202	79.7	(a)	238	5.95	4.97
204	79.3	(a)	240	4.47	3.79
206	76.7	(a)	242	3.35	2.76
208	72.7	(a)	244	2.50	1.94
210	66.6	(a)	246	1.82	1.42
212	61.4	61.3	248	1.31	0.980
214	55.9	55.6	250	0.957	0.675
216	49.3	49.0	252	0.686	0.447
218	44.2	43.3	254	0.487	0.315
220	37.7	36.6	256	0.336	0.202
222	32.4	31.2	258	0.235	0.129
224	27.6	25.9	260	0.164	0.088

(a) No detectable change in σ over the range 209-295 K

Quantum yields

Φ = 1.0 over the wavelength range 200 – 260 nm.

Comments on Preferred Values

The preferred values of the absorption cross-section at 295 K and 210 K are those reported by Gillotay and Simon.[1] Values have also been reported at 298 K by Molina *et al.*,[3] at 5 nm intervals , and by Robbins,[4] at 2 nm intervals. The agreement among these three studies is very good. Gillotay and Simon[1] have fitted their data to a polynomial to give an expression for the cross sections as a function of temperature and pressure.

The preferred values for the quantum yield are based on the study of Talukdar *et al.*[2] who showed that photolysis occurs with unit quantum efficiency by rupture of the C–Br bond.

References

1 D. Gillotay and P. C. Simon, Annal. Geophys. **6**, 211 (1988).

2 R. K. Talukdar, G. L. Vaghjiani, and A. R. Ravishankara, J. Chem. Phys. **96**, 8194 (1992).

3 L. T. Molina, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **86**, 2672 (1982).

4 D. E. Robbins, Geophys. Res. Lett. **3**, 213 (1976).