IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PI11

This data sheet updated: 15th December 2000.

$CH_2BrI + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CH_2BrI + h\nu \rightarrow CH_2Br + I$	(1)	214	559
$\rightarrow CH_2I + Br$	(2)	280	427
$\rightarrow CH_2 + IBr$	(3)	369	324

Absorption cross-section data

Wavelength range/nm	Reference	Comments
215-390	Mossinger *et al.*, 1998[1]	(a)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi_1/\Phi_2 = 6$	240-340	Lee and Bersohn, 1982[2]	(b)
$\Phi_1/\Phi_2 = 6$	248	Butler *et al.*, 1987[3]	(c)

Comments

(a) Absorption coefficients for CH_2BrI (purity 98%) were determined by diode array spectrometry with a spectral resolution of 0.6 nm. The purity of the CH_2BrI sample was 92%, the main imputities being CH_2Br_2 (6.5%) and CH_2I_2 1.5%). A correction was applied for absorption by these impurities using spectra obtained in the same spectrometer. Tabulated cross section values for the indicated range were given. Two broad absorption bands attributed to CH2BrI were observed with maxima at 215nm and 270 nm where the absorption cross sections were $\sigma = (5.67\pm0.34) \times 10^{-18}$ cm^2 molecule^{-1}and $\sigma = (2.34\pm0.14) \times 10^{-18}$ cm^2 molecule^{-1} respectively at 298 K. The temperature dependence of the absorption cross section was determined over the range 273-348K; broadening of both bands was observed giving a significant decline in σ with decreasing temperature in the tropospheric photolysis region (λ>290 nm).

(b) Photodissociation of CH_2BrI with broadband light source; dissociation fragments measured by mass spectrometry. Branching ratio for C-I and C-Br bond fission reported. These workers also reported a UV spectrum.

(c) Product state distributions measured for laser photodissociation CH_2BrI at 193.3, 210, and 248.5 nm of in a molecular beam, using TOF-MS. At 248.5 nm both C-I and C-Br bond fission occurs, with I formation dominant, producing ground state $^2P_{3/2}$ and excited state $^2P_{1/2}$ atoms in ratio of 1.0:0.75. At shorter wavelengths elimination of IBr was observed also.

Preferred Values

Absorption cross-sections for CH_2BrI at 298 K

Wavelength/nm	$10^{20}\sigma/cm^2$	$10^3B/K^{-1}$
215	567	-2.16
220	423	-0.12
225	269	1.34
230	155	2.06
235	97.9	2.05
240	80.9	1.01
245	93.7	0.0
250	125	-0.58
255	170	-1.16
260	207	-1.29
265	228	-1.45
270	229	-1.73
275	214	-1.22
280	184	-0.94
285	150	-0.53
290	110	0.1
295	82.5	0.63
300	60.6	1.03
305	42.9	1.13
310	31.4	1.41
315	23.1	1.52
320	16.8	1.71
325	11.5	2.36
330	8.02	2.99
335	5.52	3.89
340	3.50	4.79
345	2.24	5.74
350	1.41	6.73
355	0.817	9.47
360	0.498	11.5
365	0.302	11.6
370	0.165	14.3
375	0.098	17.4
380	0.070	
385	0.039	
390	0.025	

Temperature dependence given by: $\ln \sigma = \ln \sigma(298) + B(T-298/K)$

Quantum Yield

$\Phi_1 = 1.0$ over the range 290-380 nm.

Comments on Preferred Values

The.preferred values for the cross-sections and the temperature dependence are those of Mossinger *et al.*[1], which appears to be the only reported study where absolute cross section were reported. Cross- sections obtained for other halocarbons by this group agree well with other literature data and the CH_2BrI data can be considered reliable. The absorption spectrum agrees with earlier reported spectra[2,3] which show two broad bands peaking at 270 nm and 215 nm which are assigned to promotion of electrons from non-bonding orbitals in the C-I and C-Br bonds respectively.

The photodissociation of CH_2BrI via reaction (1) is expected to occur in the first absorption band with a quantum yield of unity, in line with other alkyl iodides. Studies of the photodissociation fragments[2] show that reaction (2) is dominant following absorption in the second band at 210 nm and that both processes occur in the region where the bands overlap. In the region for tropospheric photolysis (λ>290 nm) reaction (1) will dominate.

References

1 J. C. Mossinger, D. E. Shallcross, and R. A. Cox, J. Chem. Soc. Farad. Trans. **94**, 1391 (1998).

2 S. J. Lee and R. Bersohn, J. Phys. Chem. **86**, 728 (1982).

3 L. J. Butler, E. J. Hintsa, S. F. Shane, and Y. T. Lee, J. Phys. Chem. **86**, 2051 (1987).