IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PBr3

This data sheet updated: 15th December 2000.

BrO + hν → products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
BrO + hν → Br + O(^{3}P)	(1)	232	515
→ Br + O(^{1}D)	(2)	422	283

Absorption cross-section data

Wavelength range/nm	Reference	Comments
296-375	Cox, Sheppard, and Stevens, 1982[1]	(a)
312-385	Wahner *et al.*,1988[2]	(b)
338.5	Gilles *et al.*, 1997[3]	(c)

Quantum yield data

No experimental data are available.

Comments

(a) BrO radicals were produced by square-wave modulated photolysis of Br_2-O_3 mixtures and detected in absorption at 0.22 nm resolution by molecular modulation spectroscopy using a multichannel analyser to collect the signal. The absolute cross-section at 338.3 nm was determined by measuring the kinetics of BrO production and removal.

(b) BrO radicals were generated in a flowing He carrier gas by reacting Br atoms with O_3 and passed into a 1 m long absorption cell coupled to a diode array spectrometer. Spectra were recorded at 298 K and 223 K with a resolution of 0.4 nm. Absolute cross-sections were determined at 338.5 nm at both temperatures by photolysis of Br-O_3 or Br-O_2 mixtures and monitoring the kinetics of the changes in [BrO].

(c) BrO radicals were produced by pulsed laser photolysis at 193 nm of N_2O-Br_2 mixtures in an absorption cell of 87 cm path length, and detected in time resolved experiments by means of a monochromator-photomultiplier combination. Pulsed photolysis of N_2O-O_2 mixtures, detecting O_3 production by absorption at 253.7 nm, was carried out in "back-to-back"

experiments in the same system. The BrO absorption cross-sections were thus determined relative to the O_3 cross-section at 253.7nm. The absorption cross-section at the peak of the (7,0) band was measured over the temperature range 204-388 K.

Preferred Values

Absorption cross-sections of BrO at 303 K.

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
300-305	200	340-345	515
305-310	259	345-350	399
310-315	454	350-355	228
315-320	391	355-360	172
320-325	600	360-365	161
325-330	753	365-370	92
330-335	628	370-375	51
335-340	589		

Comments on Preferred Values

The BrO radical has a banded absorption spectrum in the 290-380 nm range. The values of the absorption cross-sections at the band peaks are dependent on temperature and spectral resolution. The band locations, vibrational level assignments, and the values of the absorption cross-sections at several spectral resolutions, are reported in the paper by Wahner *et al.*[2] which should be consulted for detailed information. The strongest absorption feature is the (7,0) band at 338.5 nm for which the cross-section at 0.5 nm resolution was determined to be (1.48 ± 0.14) x 10^{-17} cm^2 at 298 K. More recently a study by Gilles *et al.*[3] from the same laboratory gives a value of 1.63 x 10^{-17} cm^2. This latter value[3] is preferred. In the same study[3] Gilles *et al.* investigated the temperature dependence of the absorption cross section at the peak of the 338.5 nm band over the range 204-388 K and found that it could be represented by the relationship $\sigma_{338}/10^{-17}$ cm^2 = 3.29 – (5.58 x 10^{-3}) T.

The preferred values given in the Table are the values of the cross-section averaged over 5 nm intervals reported by Cox *et al.*[1] which are in good agreement with those of Wahner *et al.*[2] and Gilles *et al.*[3] Cox *et al.*[1] used their data to calculate a lifetime against solar photoexcitation of 30 sec for a solar zenith angle of 30 degrees. Earlier studies are discussed in previous evaluations.[4,5]

References

1 R. A. Cox, D. W. Sheppard,and M. P. Stevens, J. Photochem. **19**, 189 (1982).

2 A. Wahner, A. R. Ravishankara, S. P. Sander, and R.R. Friedl, Chem. Phys. Lett. **152**, 507 (1988).

3 M. K. Gilles, A. A. Turnipseed, J. B. Burkholder, A. R. Ravishankara, and S. Solomon, J. Phys. Chem. A **101**, 5526 (1997).

4 CODATA, 1980 (see references in Introduction).

[5] CODATA, Supplement II, 1984 (see references in Introduction).