

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PBr4

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OBrO + hv → products

Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
OBrO + hv → Br + O ₂	(1)	-52	-
→ BrO + O(³ P)	(2)	205	584

Absorption cross-section data

Wavelength range/nm	Reference	Comments
400-600	Rattigan, Jones, and Cox, 1994 ¹	(a)
385-645	Miller <i>et al.</i> , 1997 ²	(b)
390-630	Knight, Ravishankara, and Burkholder, 2000 ³	(c)

Comments

- Bromine-sensitized photodecomposition of ozone at 380 nm to 480 nm. After subtraction of absorbances due to O₃ and Br₂, the residual spectrum consisted of absorption bands from 400 nm to 600 nm superimposed on a continuum, with a maximum absorption near 505 nm. This spectrum was attributed to OBrO because of its strong resemblance to the OCIO absorption spectrum. Because absolute amounts of OBrO were not determined, absolute absorption cross-section values were not estimated. The spectral features show clear signs of broadening as T was increased from 273 K to 339 K, indicating temperature dependence of cross sections in the bands.
- Molecular bromine and products of an O₂/He discharge flowed through an absorption cell at 250 K. Strong OBrO signals were observed after pumping on the condensate collected on the cell walls. An experimental and theoretical analysis of the C(²A₂)←X(²B₁) absorption spectrum from 385 nm to 645 nm is presented, and a complete set of transition energies and assignments is given. Because absolute amounts of OBrO were not determined, absolute absorption cross-section values were not derived.
- Products of a Br₂/O₂/He discharge flow were collected in a cold trap followed by evaporation at warmer temperatures. OBrO concentrations were determined by chemical titration with excess NO yielding NO₂ + BrO, with quantitative measurement of the NO₂ product by UV absorption. Quantitative values of absorption cross-sections are reported over the wavelength

range 400 nm to 560 nm. During this study another UV absorber, assumed to be an unspecified bromine oxide Br_xO_y, was observed to originate from this OBrO source.

Preferred Values

Absorption cross-sections of OBrO at 298 K

n	(n,0,0)←(0,0,0)	10 ¹⁷ σ/cm ²	(n,1,0)←(0,0,0)	10 ¹⁷ σ/cm ²
	λ/nm		λ/nm	
0	630.4	-	622.0	-
1	606.1	-	598.4	-
2	583.8	-	576.8	-
3	563.4	1.08	556.8	1.35
4	544.4	1.45	538.5	1.74
5	527.1	1.64	521.6	1.91
6	510.7	1.77	505.5	1.96
7	495.5	1.72	490.7	1.76
8	481.2	1.67	476.9	1.51
9	468.2	1.44	464.1	1.26
10	455.8	1.21	452.2	0.96
11	444.4	1.02	440.8	0.72
12	433.7	0.79	430.4	0.49
13	423.5	0.57	420.6	0.31
14	414.1	0.40	411.0	0.22
15	405.1	0.26	402.3	0.13
16	396.4	-	394.0	-
17	388.3	-	-	-

Comments on Preferred Values

The preferred cross-section values are taken from the study of Knight *et al.*³ This is the only study in which the concentration of OBrO was quantitatively determined, thereby allowing the derivation of absolute absorption cross-section values. The uncertainty in these values is estimated to be ±30%. The transition assignments are those reported by Miller *et al.*² No quantum yield data are available. However, the threshold for photodissociation to yield BrO + O(³P) lies well beyond the wavelength of maximum absorption in the C(²A₂)←X(²B₁) envelope. By analogy with OCIO efficient photodissociation via reaction (2) is expected to occur at λ < 550 nm. The possibility of dissociation via reaction (1) at longer wavelengths cannot be ruled out, but its contribution is expected to be minor if the analogy with OCIO is used.

References

- ¹ O. V. Rattigan, R. L. Jones, and R. A. Cox, *Chem. Phys. Lett.* **230**, 121 (1994).
- ² C. E. Miller, S. L. Nikolaisen, J. S. Francisco, and S. P. Sander, *J. Chem. Phys.* **107**, 2300 (1997).
- ³ G. Knight, A. R. Ravishankara, and J. B. Burkholder, *J. Phys. Chem. A* **104**, 11121 (2000).