

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PBr8

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BrCl + hv → products

Primary Photochemical Transitions

Reaction	$\Delta H/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
BrCl + hv → Cl + Br	219	546
→ Cl(² P _{1/2}) + Br	229	521
→ Cl + Br(² P _{1/2})	263	454

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220-510	Seery and Britton, 1964 ¹	(a)
200-600	Maric, Burrows, and Moortgat, 1994 ²	(b)
190-560	Hubinger and Nee, 1995 ³	(c)

The two most recent spectra (see Comments (b) and (c)) may be conveniently compared in a Data Base coordinated by A. Nölle (UV/VIS Spectra of Atmospheric Constituents, Version 1, 1999) and administered by DLR (Deutsches Zentrum für Luft-und Raumfahrt e.V., ATMOS User Center DFD-AUC, <http://auc.dfd.dlr.de/>)

Comments

- The authors used the same apparatus for the BrCl absorption cross sections at three different Cl₂/Br₂ mixing ratios as for the measurements of both the Cl₂ and Br₂ cross sections and an equilibrium constant $K_{\text{BrCl}} = 8.1$ for the equilibrium $\text{Cl}_2 + \text{Br}_2 \rightleftharpoons 2 \text{BrCl}$ ⁴. The resulting cross sections are slightly higher than the recommended value.
- The equilibrium constant K_{BrCl} as well as the absorption spectrum of BrCl have been measured using twelve different Cl₂/Br₂ mixing ratios in nine overlapping spectral ranges of about 70 nm spectral width resulting in a spectral resolution of 0.2 nm. At least ten independent spectra were recorded at different total pressures (Cl₂, Br₂ and BrCl). The interference from a pressure-dependent component of the Br₂ vapor was negligible under the chosen experimental conditions. The value of K_{BrCl} was iteratively adjusted until minimum deviation occurred between the observed and calculated absorption spectrum of BrCl in all the regions of overlap: $K_{\text{BrCl}} = 10.1 \pm 1.1$ at 298K leads to a third law value of $\Delta H_f^0 = 14.31 \text{ kJ/mol}$.

(c) Mixtures of Cl₂ and Br₂ in 670 mbar of Ar were prepared in an evacuable gas flow line. The equilibrium concentrations have been obtained using $K_{\text{BrCl}} = 6.4^5$. The low pressures used in the present study (0.2 to 12.0 mbar) minimized the interference of Br₂ dimers. The limit to the red at $\lambda > 500$ nm is given by instrument noise. Graphical comparison between the measured spectrum and the results from the literature^{1,2} shows only minor differences. The BrCl spectrum was deconvoluted using a semi-logarithmic gaussian distribution function into four components with maxima at 228.33 (UV band), 376.39 (C¹Π₁), 454.92 (B³Π₀⁺) and 533.05 nm (A³Π₁).

No Quantum Yield Data available

Absorption Cross Sections at 298K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	2.95	410	22.39
210	4.27	420	17.78
220	6.31	430	14.45
230	6.61	440	12.59
240	5.62	450	10.72
250	4.07	460	9.33
260	5.50	470	7.94
270	1.29	480	6.31
280	0.66	490	5.01
290	0.39	500	3.39
300	0.56	510	2.63
310	1.51	520	1.66
320	4.07	530	1.10
330	9.12	540	0.66
340	17.00	550	0.41
350	28.18	560	0.25
360	34.67	570	0.144
370	41.69	580	0.832
380	39.81	590	0.0479
390	33.88	600	0.0251
400	28.18		

Comments on Preferred Values

The data of Maric *et al.*² are recommended because it is the most comprehensive data set to date available which is internally consistent using an equilibrium constant $K_{\text{BrCl}} = 10.1 \pm 1.1$ at 298K which is measured in the same study. The absorption cross sections of BrCl agree in the regions of overlap between the spectral fragments to better than $\pm 2\%$, and it is estimated that the accuracy is better than $\pm 3\%$ in the range $\lambda = 200\text{--}550$ nm. In the range 550-600 nm the agreement between spectral fragments is better than $\pm 15\%$ for an overall accuracy in this

range of better than $\pm 20\%$. Spectral deconvolution in terms of three contributing bands with maxima at 227.6, 372.5 and 442.4 nm has been obtained. Combining the values of σ_{BrCl} with the results of Sulzer and Wieland⁶ obtains the temperature and wavelength dependence of the UV/Vis absorption spectrum of BrCl. A quantum yield of unity for the dissociation of BrCl is expected.

References

- ¹ D. J. Seery and D. Britton, *J. Phys. Chem.* **68**, 2263 (1964).
- ² D. Maric, J. P. Burrows, and G. K. Moortgat, *J. Photochem. Photobiol. A: Chem.*, **83**, 179 (1994).
- ³ S. Hubinger and J. B. Nee, *J. Photochem. Photobiol. A: Chem.*, **86**, 1 (1995).
- ⁴ W. H. Evans, T. R. Munson, and D. D. Wagman, *J. Res. Natl. Bur. Std.*, **55**, 147 (1955).
- ⁵ H. C. Mattraw, C. F. Packucki, and N. J. Hawkings, *J. Chem. Phys.* **22**, 1117 (1954).
- ⁶ P. Sulzer and K. Wieland, *Helv. Phys. Acta*, **25**, 653 (1952).