IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PBr9

This data sheet updated: 15th December 2000.

$Br_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$Br_2 + h\nu \rightarrow Br(^2P_{3/2}) + Br(^2P_{3/2})$	193	620
$\rightarrow Br(^2P_{3/2}) + Br(^2P_{1/2})$	237	505

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200 – 750	Passchier, Christian, and Gregory, 1967[1]	(a)
220 - 290	Wen and Noyes, 1972[2]	(b)

Quantum yield data

See Comments on Preferred Values

Comments

(a) Spectra were obtained using a Beckman DU spectrophotometer equipped with a thermostatted optical cell. Br_2 concentrations were determined by pressure measurement or by titration with $Na_2S_2O_3$. Values of the absorption cross-section are given for temperatures of 298 K, 348 K, 423 K, 498 K, 573 K, 648 K, and 613 K. In the wavelength range 200-240 nm the measured cross sections are pressure dependent, attributed to Br_4 formation. From the pressure dependences, values of the absorption cross sections for Br_4 and Br_2 were derived in the range 200-230 nm.

(b) Spectra were obtained with a Beckman DU spectrophotometer equipped with a cell of optical path length 9.8 cm and thermostatted to 303 K. Br_2 concentrations were derived by pressure measurements. Deviations from Beer's Law which were observed, and attributed to Br_4 formation, were used to study the equilibrium between Br_2 and Br_4 and to derive values of $\sigma(Br_2)$ corrected for Br_4 absorption.

Preferred Values

Absorption cross-sections of Br_2 at 298 K.

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	0.562	350	3.48
205	0.723	355	5.63
210	0.870	360	8.65
215	0.983	365	12.7
220	1.04	370	17.8
225	1.06	375	23.9
230	1.01	380	30.7
235	0.925	385	37.9
240	0.808	390	45.1
245	0.676	395	51.8
250	0.543	400	57.4
255	0.422	405	61.6
260	0.316	410	64.2
265	0.229	415	65.1
270	0.161	420	67.7
275	0.180	425	60.8
280	0.0728	430	60.1
285	0.0471	435	57.1
290	0.02398	440	54.0
295	0.0188	445	51.2
300	0.0124	450	48.7
305	0.0101	455	46.7
310	0.0135	460	45.1
315	0.0274	465	43.8
320	0.0626	470	42.8
325	0.141	475	41.7
330	0.299	480	40.3
335	0.602	485	38.6
340	1.14	490	36.6
345	2.05	495	34.3
		500	31.8

Quantum yields

See Comments on Preferred Values

Comments on Preferred Values

Maric *et al.*[3] have evaluated the available absorption cross section data for Br_2 and have fitted the most reliable data to an expression giving σ over the range 200-600 nm as the sum of four terms each representing the contribution to σ of one of the separate overlapping absorption bands of the spectrum. The data sets selected by Maric *et al.*[3] were those of Passchier *et al.*[1] and of Wen and Noyes,[2] which cover the whole wavelength range, are in excellent agreement, and make due allowance for the deviations from Beer's Law which are observed in the 200–

300 nm region, attributed to Br_4 formation. The findings of Maric *et al*.[3] are accepted and our preferred values for the absorption cross-section at 298 K are calculated from the expression which they derived. They have also derived an extension of their expression for use at other temperatures.

In a more recent study covering the range 190-600 nm, Hubinger and Nee[4] have obtained values of σ in excellent agreement with the expression of Maric *et al*.[3] except in the 270-330 nm region where absorption cross-sections are small and only upper limits could be given.

At wavelengths longer than ~ 510 nm the spectrum consists of a banded region overlapping a continuum. High resolution spectroscopic studies[5,6] indicate rather smaller values for the contribution of the continuum absorption at long wavelengths than predicted by the expression of Maric *et al.*[3]

Absorption of radiation in the range 200-510 nm is expected to lead to bond rupture with unit quantum efficiency, giving two ground state Br atoms or $Br(^2P_{3/2}) + Br(^2P_{1/2})$, as confirmed by photofragment spectroscopic studies.[7,8] There are no direct measurements of the quantum yield but in a study of the photoinitiated bromination of ethylene Kistiakowsky and Sternberg[9] showed that the quantum yield of Br production is approximately independent of wavelength in the range 480-680 nm.

References

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