

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PBr16

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This data sheet updated: 15<sup>th</sup> December 2000.

### CH<sub>2</sub>Br<sub>2</sub> + hv → products

#### Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH <sub>2</sub> Br <sub>2</sub> + hv → CH <sub>2</sub> Br + Br	292	410

#### Absorption cross-section data

Wavelength range/nm	Reference	Comments
200-300	Molina, Molina, and Rowland, 1982 <sup>1</sup>	(a)
174-290	Gillotay, Simon, and Dierickx, 1988 <sup>2</sup>	(b)
215-300	Mössinger, Shallcross, and Cox, 1998 <sup>3</sup>	(c)

#### Quantum yield data

No experimental data are available.

#### Comments

- The cross-sections were measured using a double beam spectrophotometer equipped with 10 cm and 180 cm cells. Pressures in the range 8-52 mbar were used.
- Spectra were obtained using a thermostatted absorption cell with a single pass optical path of 2 m coupled to a monochromator capable of a maximum resolution of 0.015 nm. Pressures of CH<sub>2</sub>Br<sub>2</sub> used covered the range  $5 \times 10^{-2}$  – 47 mbar. Spectra were recorded at 295 K, 270 K, 250 K, 230 K, and 210 K.
- Spectra were obtained using a thermostatted absorption cell of optical path length 100 cm coupled to a double beam optical system giving a resolution of ~ 0.6 nm. Pressures used were in the range 0.13-53 mbar. Absorption measurements were made at 348 K, 328 K, 298 K, 273 K, and 250 K. At each wavelength the temperature dependence of the cross-sections was expressed as  $\ln \sigma_T = \ln \sigma_{298\text{ K}} + B(T - 298)$  and values of B were derived.

## Preferred Values

### Absorption cross-sections of CH<sub>2</sub>Br<sub>2</sub> at 298 K and 210 K.

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$		$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	
	298 K	210 K		298 K	210 K
200	226	223	255	14.1	8.51
205	215	206	260	6.61	3.38
210	235	240	265	3.03	1.34
215	263	325	270	1.34	0.506
220	272	356	275	0.514	0.199
225	247	318	280	0.255	0.0773
230	196	239	285	0.114	0.0324
235	139	154	290	0.0499	0.0140
240	88.6	86.1	295	0.0165	0.0049
245	51.9	43.6	300	0.006	0.0013
250	28.0	19.7			

#### Comments on Preferred Values

The preferred values for the absorption cross-sections at 298 K are the means of the values reported by Molina *et al.*,<sup>1</sup> Gillotay *et al.*<sup>2</sup> and Mössinger *et al.*<sup>3</sup> The agreement among the three studies<sup>1-3</sup> over the wavelength range of the preferred values is excellent. The temperature dependence of  $\sigma$  over the range 210-295 K has been studied by Gillotay *et al.*<sup>2</sup> and over the range 250-348 K by Mössinger *et al.*<sup>3</sup> The results agree well in the region where they overlap and both find that  $\sigma$  increases with decreasing temperature at the absorption band maximum (219 nm) but shows a decrease with temperature decrease in the long wavelength tail of the spectrum. The preferred values at 210 K are those of Gillotay *et al.*<sup>2</sup> which are in very good agreement with the values calculated from the expression and temperature coefficients of Mössinger *et al.*,<sup>3</sup> based on their measurements in the range 250-348 K.

There are no quantum yield measurements but photolysis is expected to occur with unit quantum efficiency by C-Br bond rupture.

#### References

- <sup>1</sup> L. T. Molina, M. J. Molina, and F. S. Rowland, *J. Phys. Chem.* **86**, 2672 (1982).
- <sup>2</sup> D. Gillotay, P.C. Simon, and L. Dierickx, *Aeron. Acta* **35**, 1 (1988).
- <sup>3</sup> J. C. Mössinger, D. E. Shallcross, and R. A. Cox, *J. Chem. Soc. Faraday Trans.* **94**, 1391 (1998).