

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PBr15

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CF₂BrCF₂Br (Halon-2402) + hv → products

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₂ BrCF ₂ Br + hv → CF ₂ BrCF ₂ + Br	280 (est)	427

Absorption cross-section data

Wavelength range/nm	Reference	Comments
170-302	Gillotay, Simon, and Dierickx, 1988 ¹	(a)
190-320	Burkholder <i>et al.</i> , 1991 ²	(b)
190-304	Orkin and Kasimovskaya, 1995 ³	(c)

Quantum yield data

No experimental data are available.

Comments

- 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. Spectra were recorded at 295 K, 270 K, 250 K, 230 K, and 210 K. The data were fitted to a polynomial expression giving the cross sections as a function of temperature and pressure.
- Spectra were obtained using a thermostatted absorption cells with single pass optical paths of 98.1 cm and 150 cm, coupled to spectrographs having resolutions in the range 0.4-0.5 nm. Spectra were recorded at 296 K, 270 K, 250 K, 230 K, and 210 K. The data were fitted to a polynomial expression giving the cross sections as a function of temperature and pressure.
- Spectra were obtained using a cell thermostatted at 295 K with a single path optical length of 14.0 cm and coupled to a double beam spectrophotometric system. Sample pressures in the range 0.65–160 mbar were used.

Preferred Values

Absorption cross-sections of CF₂BrCF₂Br at 295 K and 210 K.

λ/nm	10 ²⁰ σ/cm ²		λ/nm	10 ²⁰ σ/cm ²	
	295 K	210 K		295 K	210 K
190	108	119	240	13.4	11.5
192	114	124	242	10.7	8.95
194	119	128	244	8.47	6.89
196	123	131	246	6.69	5.25
198	125	133	248	5.23	2.95
200	125	133	250	4.05	2.93
202	125	132	252	3.09	2.15
204	121	129	254	2.36	1.56
206	117	125	256	1.77	1.13
208	112	119	258	1.32	0.807
210	105	112	260	0.978	0.576
212	98.6	104	262	0.724	0.391
214	94.5	96.1	264	0.535	0.275
216	83.4	85.0	266	0.394	0.191
218	75.6	79.0	268	0.290	0.134
220	67.8	70.3	270	0.212	0.093
222	60.2	62.0	272	0.155	
224	53.0	54.3	274	0.112	
226	46.2	46.8	276	0.082	
228	40.0	40.1	278	0.060	
230	34.2	33.9	280	0.044	
232	29.0	27.9			
234	24.3	22.6			
236	20.1	18.2			
238	16.5	14.5			

Comments on Preferred Values

The preferred values for the absorption cross-sections at 295 K are the means of the values reported by Gillotay *et al.*,¹ Burkholder *et al.*,² and Orkin and Kasimovskaya.³ Values at 5 nm intervals have also been reported by Molina *et al.*⁴ The agreement among the four studies¹⁻⁴ over the wavelength range of the preferred values is very good. The temperature dependence down to 210 K has been studied by Gillotay *et al.*,¹ and Burkholder *et al.*² There are significant differences between the two studies.^{1,2} Close to the absorption peak (~200 nm) Burkholder *et al.*¹ report a 20 % increase in the absorption cross-section in going from 295 K to 210 K, whereas Gillotay *et al.*² report a small decrease. Furthermore, at 210 K the values of the cross-section obtained by Gillotay *et al.*¹ are only ~4% lower than those of Burkholder *et al.*² at short wavelengths but this difference increases in going to longer wavelengths, reaching ~40% at 270 nm. Provisionally, the preferred values at 210 K are taken as the mean of the values of Gillotay *et al.*¹ and Burkholder *et al.*²

Photolysis is expected to occur with unit quantum efficiency by rupture of the C-Br bond to give CF₂BrCF₂ + Br. CF₂BrCF₂Br has been estimated to have a tropospheric lifetime against direct solar photolysis of 34 years.²

References

- ¹ D. Gillotay, P. C. Simon, and L. Dierickx, *Aeronomica Acta* **335**, 1 (1988).
- ² J. B. Burkhokder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5025 (1991).
- ³ V. L. Orkin and E. E. Kasimovskaya, *J. Atmos. Res.* **21**, 1 (1995).
- ⁴ L. T. Molina, M. J. Molina, and F. S. Rowland, *J. Phys. Chem.* **86**, 2672 (1982).