IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PBr13

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CF_2Br_2 (Halon-1202) + hν → products

Primary photochemical processes

Reaction		ΔH°/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CF_2Br_2 + h\nu \rightarrow CF_2Br + Br$	(1)	280 (est)	427
$\rightarrow CF_2 + Br + Br$	(2)	419	286

Absorption cross-section data

Wavelength range/nm	Reference	Comments
170-302	Gillotay and Simon, 1989[1]	(a)
190-320	Burkholder *et al.*, 1991[2]	(b)
190-304	Orkin and Kasimovskaya, 1995[3]	(c)

Quantum yield data

Measurement	Wavelength /nm	Reference	Comments
$\Phi(CF_2O) = 1.14$	206.2	Molina and Molina, 1983[4]	(d)
$\Phi(Br_2) = 1.11$			
$\Phi(-CBr_2F_2) = 1.12$			
$\Phi(CF_2O) = 1.03$	247.7		
$\Phi(Br_2) = 0.99$			
$\Phi(-CBr_2F_2) = 1.05$	302.4		
$\Phi(CF_2O) = 1.23$			
$\Phi(Br_2) = 1.28$			
$\Phi(Br) = 1.96 \pm 0.25$	193	Talukdar *et al.*, 1992[5]	(e)
$\Phi(Br) = 1.63 \pm 0.19$	222		
$\Phi(Br) = 1.01 \pm 0.15$	248		
$\Phi(CF_2) = 1.11 \pm 0.22$	193	Talukdar *et al.*, 1996[6]	(e)
$\Phi(CF_2) = 1.18 \pm 0.30$	193		

Comments

(a) 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 CF_2Br_2 used covered the range 0.04 – 308 mbar. 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.

(b) Spectra were obtained using 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.

(c) 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 0.013–1 bar were used.

(d) Product study on photolysis of CF_2Br_2-air mixtures at 1 bar. The only photolysis products found were CF_2O and Br_2. The CF_2O and CBr_2F_2 concentrations were monitored by FTIR, and the Br_2 concentrations by UV absorption.

(e) Both of the studies of Talukdar *et al.*[5,6] employed basically the same technique. Pulsed laser photolysis of flowing CF_2Br_2-diluent (He, N_2, or Ar) mixtures was used with a small amount of H_2 added to ensure rapid quenching of the $Br(^2P_{1/2})$ produced to $Br(^2P_{3/2})$. $Br(^2P_{3/2})$ was detected by resonance fluorescence and CF_2 by UV absorption. The two values of $\Phi(CF_2)$ cited were obtained by monitoring $[CF_2]$ at 248.7 and 258.3 nm. The $Br(^2P_{3/2})$ measurements were calibrated by CH_3Br photolysis at the same wavelength for which a quantum yield of unity was assumed. The CF_2 measurements were calibrated using C_2F_4 photolysis taking a quantum yield for CF_2 production at 193 nm of 2.

Preferred Values

Absorption cross-sections of CF_2Br_2 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	117	130	250	58.3	55.3
192	110	122	252	46.5	39.1
194	102	110	254	36.8	29.9
196	91.4	97.8	256	28.9	22.6
198	82.1	86.3	258	22.4	17.0
200	74.8	78.4	260	17.3	12.5
202	71.7	74.5	262	13.1	9.17
204	73.4	77.1	264	9.90	6.66
206	80.9	85.2	266	7.47	4.81
208	92.3	100	268	5.59	3.44
210	110	120	270	4.17	2.44
212	134	145	272	3.08	1.72
214	155	173	274	2.27	1.21
216	180	202	276	1.66	0.844
218	205	230	278	1.21	0.588
220	226	254	280	0.888	0.406
222	244	273	282	0.647	0.281
224	253	282	284	0.470	0.194
226	257	283	286	0.336	0.129

228	253	277	288	0.245	0.0891
230	245	264	290	0.177	0.0616
232	230	245	292	0.128	0.405
234	212	222	294	0.093	0.277
236	192	197	296	0.067	0.185
238	170	171	298	0.049	0.127
240	147	145	300	0.035	0.0083
242	126	121	302	0.025	0.0056
244	106	99.3	304	0.018	0.0011
246	87.8	86.4	306	0.013	
248	72.0	64.1	308	0.009	

Quantum yields

$\Phi = 1.0$ over the range 200-310 nm.

Comments on Preferred Values

The preferred values for the absorption cross-sections at 295 K are the means of the values reported by Gillotay and Simon,[1] Burkholder *et al.*,[2] and Orkin and Kasimovskaya.[3] Values at 5 nm intervals have also been reported by Molina *et al.*[7] The agreement among the four studies[1-3,7] over the wavelength range of the preferred values is very good although discrepancies appear at longer wavelengths. The temperature dependence down to 210 K has been studied by Gillotay and Simon[1] and Burkholder *et al.*[2] There is only fair agreement between the two studies. At $\lambda > 250$ nm both report a decrease in absorption as the temperature is lowered,[1,2] and near the absorption peak (about 230 nm) both studies find an 11% increase in absorption in going to the lowest temperature. However, although the values of σ from the two studies are in good agreement close to the absorption maximum they steadily diverge on moving to longer and shorter wavelengths reaching a 30% difference at 190 nm and a factor of 2 at 300 nm. Provisionally, the preferred values at 210 K are taken as the mean of the values from Gillotay and Simon[1] and Burkholder *et al.*[2]

Molina and Molina[4] found that the only products of photolysis of CF2Br$_2$-air mixtures at a pressure of 1 bar were CF_2O and Br_2 and concluded that the quantum yield for photodissociation of CBr_2F_2 was unity over the wavelength range 200-300 nm. This is supported by the findings of Talukdar *et al.*[5,6] The preferred values for the quantum yields are based on the studies of Molina and Molina[4] and Talukdar *et al.*[5,6] Molecular beam[8] and spectroscopic studies[9,10] at 248 nm have detected the transient CF_2Br and confirm that the primary process is rupture of the C-Br bond.

Because its absorption extends into the 290-310 nm wavelength range, CF_2Br_2 has a short tropospheric lifetime against direct solar photoexcitation, of about 3 years.

References

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