IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PBr12

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CF_2ClBr (Halon-1211) + hν → products

Primary photochemical processes

Reaction		$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CF_2ClBr + h\nu \rightarrow CF_2 + ClBr$	(1)	269	445
$\rightarrow CF_2Cl + Br$	(2)	271	441
$\rightarrow CF_2Br + Cl$	(3)	348 (est)	344
$\rightarrow CF_2 + Cl + Br$	(4)	488	245

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
$\Phi(Cl) = 1.03 \pm 0.14$	193	Talukdar *et al.*, 1996[4]	(d)
$\Phi(Br) = 1.04 \pm 0.14$	193		
$\Phi(CF_2) = 0.9 \pm 0.2$	193		
$\Phi(Cl) = 0.27 \pm 0.04$	222		
$\Phi(Br) = 0.86 \pm 0.04$	222		
$\Phi(Cl) = 0.18 \pm 0.03$	248		
$\Phi(Br) = 0.75 \pm 0.12$	248		

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_2ClBr used covered the range 0.13 – 600 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) Quantum yields were determined by photolysis of CF_2ClBr and a reference compound in "back-to-back" experiments. For $\Phi(Cl)$ determinations at 193 nm the reference compound was HCl and at 222 nm and 248 nm Cl atom yields were measured relative to those at 193nm. CH_3Br and C_2F_4 were used as reference compounds for measuring the yields of Br and CF_2 respectively. [Cl] and [Br] were monitored by RF and $[CF_2]$ by long path absorption. $[CF_2ClBr]$ and [HCl] were determined by UV absorption and $[C_2F_4]$ by pressure measurements.

Preferred Values

Absorption cross-sections of CF_2ClBr at 295 K and 210 K.

λ/nm	10^{20} σ/cm^2		λ/nm	10^{20} σ/cm^2	
	295 K	210K		295K	210 K
190	47.4	50.5	240	17.7	15.6
192	57.7	64.5	242	14.5	12.6
194	70.3	79.3	244	11.9	9.97
196	83.0	94.3	246	9.66	7.82
198	95.6	106	248	7.77	6.13
200	109	120	250	6.23	4.70
202	117	130	252	4.93	3.57
204	121	132	254	3.89	2.72
206	122	134	256	3.05	2.02
208	121	133	258	2.37	1.51
210	117	129	260	1.83	1.11
212	112	123	262	1.41	0.811
214	104	115	264	1.07	0.589
216	96.2	106	266	0.816	0.425
218	87.8	96.2	268	0.618	0.307
220	79.0	86.0	270	0.465	0.216
222	70.3	75.7	272	0.349	0.153
224	62.1	66.2	274	0.259	0.107
226	54.3	57.2	276	0.190	0.0742
228	47.3	49.0	278	0.139	0.0516
230	40.9	41.3	280	0.103	0.0355
232	35.2	34.6	282	0.075	0.0244
234	29.9	28.8	284	0.055	0.0167
236	25.4	23.7	286	0.040	0.0106
238	21.3	19.4	288	0.029	0.00721

Quantum yields

$\Phi = 1.0$ over the range 200-300 nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K are the mean of the values obtained in the studies of Gillotay and Simon,[1] Burkholder *et al*.,[2] and Orkin and Kasimovskaya.[3] Values have also been reported by Molina *et al*.[5] at 5 nm intervals, and by Giolondo *et al.*[6] at 10 nm intervals. The agreement among these five studies[1-3,5,6] at 295 K, over the wavelength range of the preferred values, is excellent. The temperature dependence of the cross-sections down to 210 K has been studied by Gillotay and Simon[1] and by Burkholder *et al.*[2] and in both cases polynomial expressions were derived giving the cross-sections as a function of temperature and wavelength. At $\lambda > 234$ nm both studies reported a decrease in absorption as the temperature was lowered. But near the absorption peak (~ 205 nm) Burkholder *et al.*[2] found the cross-sections to be independent of temperature, while Gillotay and Simon[1] found the absorption to increase with decreasing temperature, with a 20% increase at the lowest temperature studied. Furthermore, at 210 K the values of σ of Gillotay and Simon[1] are larger than those of Burkholder *et al.*[2] by ~13% at 288 nm, increasing to ~30% at 190 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]

Talukdar *et al.*[4] measured the quantum yields of CF_2, Cl, and Br at 193 nm and found that the CF_2ClBr was photodissociated to give CF_2 with a quantum yield of unity, probably by initial production of CF_2Cl which was not collisionally stabilized under their conditions but went on to give $CF_2 + Cl$. Baum and Huber,[7] in a photofragment translational spectroscopy study, also found that at 193 nm the dominant primary process is rupture of the C-Br bond followed by decomposition of the energised CF_2Cl fragment, and a minor pathway involving initial rupture of the C-Cl bond was also detected. At longer wavelengths photodissociation by breaking of a C-halogen bond is expected to persist with unit quantum efficiency.

CF_2ClBr has been estimated to have a tropospheric lifetime against direct solar photoexcitation of 15 to 20 years.[2,5]

References

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