IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PBr14

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$CHBr_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CHBr_3 + h\nu \rightarrow CHBr_2 + Br$	276	433

Absorption cross-section data

Wavelength range/nm	Reference	Comments
170-310	Gillotay and Simon, 1989[1]	(a)
286-362	Moortgat, Meller, and Schneider, 1993[2]	(b)

Quantum yield data

No experimental data are available.

Comments

(a) Two different techniques were used. One employed a cell with a fixed optical path of 2 m and an evacuated monochromator capable of reaching wavelengths down to 170 nm. In the other a multiple reflection cell with optical paths up to 5 m was used. In both cases the cells were thermostatted and measurements were made in the range 295-240 K.

(b) Measurements were made using two pieces of apparatus. In one a cell of 63 cm fixed path length was used and measurements made at 296 K. The other contained multiple pass optics with a total path length of 980 cm. The latter system was used for measurements at 296 K, 286 K, 266 K, and 256 K.

Preferred Values

Absorption cross-sections of $CHBr_3$ at 296 K and 210 K.

λ/nm	10^{20} σ/cm^2		λ/nm	10^{20} σ/cm^2	
	296 K	210 K		296 K	210 K
190	399	393	270	30.8	21.1
192	360	351	272	24.8	16.5
194	351	353	274	19.8	12.8
196	366	383	276	15.8	9.94
198	393	422	278	12.5	7.66
200	416	466	280	9.88	5.88
202	433	475	282	7.77	4.50
204	440	474	284	6.10	3.42
206	445	467	286	4.81	2.60
208	451	471	288	3.75	1.97
210	468	490	290	2.88	1.49
212	493	522	292	2.22	1.05
214	524	551	294	1.70	0.757
216	553	593	296	1.28	0.547
218	574	621	298	0.951	0.395
220	582	633	300	0.719	0.285
222	578	623	302	0.530	0.206
224	558	597	304	0.394	0.149
226	527	562	306	0.298	0.107
228	487	516	308	0.226	0.078
230	441	465	310	0.171	0.060
232	397	409	312	0.127	0.040
234	362	362	314	0.095	0.029
236	324	324	316	0.071	0.021
238	295	295	318	0.053	0.015
240	273	272	320	0.039	0.011
242	253	250	322	0.029	0.0079
244	234	224	324	0.021	0.0057
246	214	202	326	0.016	0.0041
248	194	178	328	0.009	0.0030
250	174	157	330	0.009	0.0022
252	158	138	332	0.007	0.0016
254	136	116	334	0.005	0.0011
256	116	96.2	336	0.004	0.00081
258	98.6	79.5	338	0.003	0.00059
260	82.8	64.7	340	0.002	0.00042
262	68.9	52.5			
264	56.9	42.2			
266	46.7	33.7			
268	38.0	26.7			

Comments on Preferred Values

There have been two studies of the absorption cross-sections of $CHBr_3$. Gillotay *et al.*[1] reported values over the wavelength range 170-310 nm and the temperature range 295-240 K; Moortgat *et al.*[2] reported values over the range 245-360 nm and the temperature range 296-256 K. In the region where the measurements overlap, the agreement is very good. The preferred values at 296 K are those reported by Gillotay *et al.*[1] over the wavelength range 190-284 nm and those reported by Moortgat *et al.*[2] at longer wavelengths. The preferred values at 210 K are those of Gillotay *et al.*[1] over the range 190-298 K, which they obtained by extrapolation of their higher temperature results, and those over the range 290-340 K are from the expression, $\ln \sigma(\lambda,T) = (0.0618350 - 0.000241014\ \lambda)(273-T) - (2.37616 + 0.1475688\ \lambda)$, which was derived by Moortgat *et al.*[2] from a fit to the combined data of their study and that of Gillotay *et al.*[1] It is valid in the wavelength range 290-340 nm and the temperature range 300-210 K.

Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Br bond to yield $CHBr_2 + Br$.

References

1 D. Gillotay, A. Jenouvrier, B. Coquart, M. F. Merrienne, and P. C. Simon, Planet. Space Sci. **37**, 1127 (1989).

2 G. K. Moortgat, R. Meller, and W. Schneider, pp.359-369, in "*The Tropospheric Chemistry of Ozone in the Polar Regions*," H. Niki and K. H. Becker, editors, NATO ASI Series, Volume 17, Springer-Verlag, Berlin, 1993.