IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PCl20

The citation for this data sheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Wallington, T. J.: Atmos. Chem. Phys., 9, 4141, 2008; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.

This datasheet last evaluated: June 2015; last change in preferred values: December 2005.

$CH_3CCl_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CCl_3 + h\nu \rightarrow CH_3CCl_2 + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for CH_3CCl_3 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
182	315	a	210	24.0	19.8
184	280	a	212	16.8	13.2
186	250	a	214	12.0	8.8
188	220	a	216	8.6	6.1
190	192	a	218	6.0	4.2
192	163	a	220	4.1	2.9
194	140	a	222	2.9	1.2
196	118	a	224	2.0	1.2
198	99	a	226	1.5	0.76
200	81	a	228	1.0	0.51
202	66	64	230	0.70	0.33
204	52	49	232	0.49	0.18
206	40	36	234	0.33	0.11
208	31	26	236	0.23	0.064
			238	0.15	0.036
			240	0.10	0.024

(a) No temperature dependence observed.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K and at 210 K are the values reported by Vanlaethem-Meuree et al. (1979), who determined absorption cross-section values at 295 K, 270 K, 250 K, 230 K and 210 K for the wavelength range 180–240 nm. These values (Vanlaethem-Meuree et al., 1979) are preferred over the substantially higher values reported by Hubrich and Stuhl (1980), in which study a correction was required for the presence of the UVabsorbing stabilizer 1,4-dioxane. In a recent study, Nayak et al. (1995) reported measurements in the gas phase (160–240 nm) and the liquid phase (235–260 nm) over the temperature range 220–330 K.

A wavelength shift procedure was used to convert the liquid-phase values into effective gas-phase values at the long wavelengths. The reported room temperature values of Nayak et al. (1995) are in good agreement (within 15%) with those of Vanlaethem-Meuree et al. (1979) in the range 210–240 nm, whereas in the 180–210 nm range they are 15% to 30% higher. Low temperature results are in relatively good agreement up to 230 nm. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield $CH_3CCl_2 + Cl$.

References

Hubrich, C. and Stuhl, F.: J. Photochem. 12, 93, 1980.

Nayak, A. K., Kurylo, M. J. and Fahr, A.: J. Geophys. Res. 100, 11185, 1995.

Vanlaethem-Meuree, N., Wisemberg,J. and Simon, P. C.: Geophys. Res. Lett. 6, 451, 1979.