

IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet PCI20

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$\text{CH}_3\text{CCl}_3 + h\nu \rightarrow \text{products}$

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{CCl}_3 + h\nu \rightarrow \text{CH}_3\text{CCl}_2 + \text{Cl}$	335 (est)	360

Preferred Values

Absorption cross-sections for CH_3CCl_3 at 295 K and 210 K

λ/nm	$10^{20} \sigma/\text{cm}^2$		λ/nm	$10^{20} \sigma/\text{cm}^2$	
	295 K	210 K		295 K	210 K
182	315	a	210	24.0	19.8
4	280	a	2	16.8	13.2
6	250	a	4	12.0	8.8
8	220	a	6	8.6	6.1
190	192	a	8	6.0	4.2
2	163	a	220	4.1	2.9
4	140	a	2	2.9	1.2
6	118	a	4	2.0	1.2
8	99	a	6	1.5	0.76
200	81	a	8	1.0	0.51
2	66	64	230	0.70	0.33
4	52	49	2	0.49	0.18
6	40	36	4	0.33	0.11
8	31	26	6	0.23	0.064
			8	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.*¹ 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 values¹ are preferred over the substantially higher values reported by Hubrich and Stuhl,² in which study a correction was required for the presence of the UV-absorbing stabilizer 1,4-dioxane. In a recent study Nayak *et al.*³ 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 values³ are in good agreement (within 15%) with those of Vanlaethem-Meuree *et al.*¹ 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 $\text{CH}_3\text{CCl}_2 + \text{Cl}$.

References

- ¹ N. Vanlaethem-Meuree, J. Wisenberg, and P. C. Simon, *Geophys. Res. Lett.* **6**, 451 (1979).
- ² C. Hubrich and F. Stuhl, *J. Photochem.* **12**, 93 (1980).
- ³ A. K. Nayak, M. J. Kurylo, and A. Fahr, *J. Geophys. Res.* **100**, 11185 (1995).