

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PCI12

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CH₃Cl + hv → products

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH ₃ Cl + hv → CH ₃ + Cl	349	343

Preferred Values

Absorption cross-sections for CH₃Cl at 295 K and 210 K

λ/nm	$10^{20} \sigma/\text{cm}^2$			
	295K ^a			
174	111	8	2.66	2.43
6	93.8	200	1.76	1.51
8	76.6	2	1.13	0.93
180	60.7	4	0.750	0.573
2	46.7	6	0.483	0.345
4	35.0	8	0.318	0.212
6	25.5	210	0.206	0.130
8	18.2	2	0.132	0.080
190	12.7	4	0.086	0.047
2	8.72	6	0.055	0.027
4	5.88			
6	4.01			

^aNo temperature dependence at $\lambda < 198$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K and at 210 K are those reported by Simon *et al.*¹ This publication¹ reports the results of the most comprehensive study of the temperature dependence. These values are in very good agreement with the room temperature values reported by Robbins,² and are in reasonable agreement with the results of Hubrich *et al.*³ who also made low temperature measurements. In the wavelength region 180-216 nm, photolysis occurs with unit quantum efficiency by breaking of the C-Cl bond to yield CH₃ + Cl. Photochemistry at shorter wavelengths is discussed by Shold and Rebbert.⁴

References

- ¹ P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisenberg, *J. Atmos. Chem.* **7**, 107 (1988).
- ² D. E. Robbins, *Geophys. Res. Lett.* **3**, 213 (1976); erratum *op. cit.* **3**, 757 (1976).
- ³ C. Hubrich, C. Zetsch, and F. Stuhl, *Ber. Bunsenges. Phys. Chem.* **81**, 437 (1977).
- ⁴ D. M. Shold and R. E. Rebbert, *J. Photochem.* **9**, 499 (1978).