

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PC116

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CFCl₃ (CFC-11) + hv → products

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CFCl ₃ + hv → CFCl ₂ + Cl (1)	317	377
→ CFCl + 2Cl (2)	558	214

Preferred Values

Absorption cross-sections for CFCl₃ at 295 K and 210 K

λ/nm	$10^{20} \sigma/\text{cm}^2$		λ/nm	$10^{20} \sigma/\text{cm}^2$	
	295K	210 K ^a		295 K	210 K
174	313	-	210	14.8	9.9
6	324	-	2	10.5	6.63
8	323	-	4	7.56	4.31
180	314	-	6	5.38	2.78
2	296	-	8	3.79	1.77
4	272	-	220	2.64	1.13
6	243	230	2	1.82	0.71
8	213	202	4	1.24	0.45
190	179	170	6	0.84	0.29
2	154	141	8	0.56	0.19
4	124	115	230	0.37	0.12
6	99.1	90.5	235	0.126	
8	78.0	71.8	240	0.046	
200	64.5	55.8	245	0.017	
2	50.0	42.0	250	0.006	
				6	
4	37.4	30.0	255	0.003	
				4	
6	28.0	21.6	260	0.001	

^aNo temperature dependence observed at $\lambda \leq 184$ nm.

Quantum yields for CFCl_3 photolysis at 298 K

$\Phi(1) = 1$ at $\lambda > 180$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections for 174-250 nm at 295 K and 210 K are the values reported by Simon *et al.*¹ This publication reports the results of the most comprehensive study of the temperature dependence.¹ For $\lambda > 230$ nm, the absorption cross-section values are those reported by Hubrich and Stuhl.² The values are in good agreement with those recommended in our previous evaluation, CODATA, 1982,³ where a detailed discussion of earlier work can be found. They also agree with the recommendations of NASA⁴ which include an expression for the temperature dependent cross-sections applicable over the range 190-210 nm:

$$\sigma_T = \sigma(218)\exp(4.1 \times 10^{-4}(\lambda - 184.9)(T - 298)) \quad [\lambda \text{ in nm; } T \text{ in K}].$$

Felder and Demuth⁵ studied laser photodissociation of CFCl_3 at 193 nm using TOF-MS to investigate the nature and energetics of the photofragments. At this wavelength dissociation occurs exclusively to yield $\text{CFCl}_2 + \text{Cl}$ products. This result is in conflict with the earlier conclusions of Rebbert and Ausloos⁶ that $\Phi(2)$ increases from 0.06 at 220 nm to 0.43 at 170 nm. This result from indirect experiments must now be considered dubious.

References

- ¹ P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisenberg, *J. Atmos. Chem.* **7**, 107 (1988).
- ² C. Hubrich and F. Stuhl, *J. Photochem.* **12**, 93 (1980).
- ³ CODATA, Supplement I, 1982 (see references in Introduction).
- ⁴ NASA Evaluation No. 12, 1997 (see references in Introduction).
- ⁵ P. Felder and C. Dermuth, *Chem. Phys. Lett.* **208**, 21 (1993).
- ⁶ R. E. Rebbert and P. J. Ausloos, *J. Photochem.* **4**, 419 (1975).