IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PCl15

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CF_2Cl_2 (CFC-12) + hν → products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_2Cl_2 + h\nu$	→ $CF_2Cl + Cl$ (1)	346	346
	→ $CF_2 + 2Cl$ (2)	542	221

Preferred Values

Absorption cross-sections for CF_2Cl_2 at 295 K and 210 K

λ/nm	10^{20} σ/cm^2		λ/nm	10^{20} σ/cm^2	
	295K	210 K[a]		295 K	210 K
174	162	-	200	8.89	5.11
6	181	-	2	5.51	2.97
8	187	-	4	3.44	1.69
180	179	-	6	2.09	0.99
2	160	-	8	1.27	0.56
4	134	-	210	0.76	0.32
6	107	-	2	0.45	0.18
8	82.8	79.3	4	0.27	0.10
190	63.2	52.9	6	0.16	0.058
2	45.5	35.8	8	0.10	0.033
4	31.5	22.8	220	0.060	0.018
6	21.1	14.4	2	0.036	0.010
8	13.9	8.8	4	0.022	0.006
			6	0.013	0.003

[a]No significant temperature dependence observed at λ ≤ 186 nm.

Quantum yields for CF_2Cl_2 photolysis at 298 K

$\Phi(1) = 1$ over the range 190-225 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 publication reports the results of the most comprehensive study of the temperature dependence.[1] The values at room temperature are in good agreement with those recommended in our previous evaluation, CODATA, 1980,[2] where a detailed discussion of earlier work can be found. They also agree with the recommendations of NASA[3] which include an expression for the temperature dependent cross-sections applicable over the range 190-210 nm:

$\sigma_T = \sigma(218)\exp(4.1\times10^{-4}(\lambda-184.9)(T-298))$ [λ in nm; T in K].

Baum and Huber[4] studied laser photodissociation of CF_2Cl_2 at 193 nm, with photoproducts investigated by TOF-MS. Results show exclusive dissociation to $CF_2Cl + Cl$, with the CF_2Cl fragment containing insufficient energy for prompt dissociation to produce a second Cl atom. This is contrary to the earlier suggestion by Rebbert and Ausloos[5] that formation of 2 Cl atoms occurred with increasing tendency at wavelengths < 230 nm. For the purposes of atmospheric photolysis a value of $\Phi(1) = 1$ is recommended.

References

1 P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, J. Atmos. Chem. **7**, 107 (1988).

2 CODATA, 1980 (see references in Introduction).

3 NASA Evaluation No. 12, 1997 (see references in Introduction).

4 G. Baum and R. J. Huber, Chem. Phys. Lett. **203**, 261 (1993).

5 R. E. Rebbert and P. J. Ausloos, J. Photochem. **4**, 419 (1975).