IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PCl14

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CHF_2Cl (HCFC-22) + hν → products

Primary photochemical processes

Reaction		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
CHF_2Cl + hν	→ CHF_2 + Cl (1)	327	327
	→ $CClF_2$ + H (2)	423	283
	→ CF_2 + HCl (3)	207	577

Preferred Values

Absorption cross-sections for CHF_2Cl at 298 K and 210 K

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²	
	298K[a]		298 K	210 K
174	5.72	188	0.372	0.372
176	4.04	190	0.245	0.242
178	2.76	192	0.156	0.148
180	1.91	194	0.103	0.093
182	1.28	196	0.072	0.062
184	0.842	198	0.048	0.039
186	0.576	200	0.032	0.0159
		202	0.022	0.0159
		204	0.014	0.0096

[a]No temperature dependence at λ < 188 nm.

Quantum yields for CHF_2Cl photolysis

Φ(1) = 0.84; Φ(2) = 0.16 at 193 nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are those reported by Simon *et al*.[1] In the same study[1] the temperature dependence down to 210 K has been reported, with the values at the shorter wavelengths being temperature-independent within the precision of the measurements. The values at longer wavelengths show a decrease as the temperature is lowered.[1] These results are in reasonable agreement with thhose of earlier studies cited in NASA, 1997.[2] Melchior *et al*.[3] studied the photodissociation of CHF_2Cl at 193 nm using TOF-MS combined with 2+1 REMPI to detect products. Photolysis by 2 channels, C-Cl and C-H bond rupture, was observed; HCl elimination was not found. C-Cl rupture is the main channel. The minor channel yield was $\Phi_H/\Phi_{total} = 0.16 \pm 0.05$. This work forms the basis of the recommended values at 193 nm. The quantum yields are likely to be wavelength dependent with $\Phi(1)$ increasing towards 1.0 at the absorption threshold near 205 nm.

References

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

[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
A. Melchior, P. Knupfer, I. Bar, S. Rosenwaks, T. Laurent, H.-R. Volpp and J. Wolfrum, J. Phys. Chem. **100**, 13375 (1996).