IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PCl29

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C(O)FCl + hν → products

Primary photochemical processes

Reaction			$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
C(O)FCl + hν	→ FCO + Cl	(1)	396	302
	→ ClCO + F	(2)	485	247
	→ CO + F + Cl	(3)	517	231
	→ CFCl + O(^{3}P)	(4)	707	169

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi_1 + \Phi_3 = 0.98 \pm 0.09$	193	Hermann et al., 1994	(a,b,c)
$\Phi_1 + \Phi_3 = 0.90 \pm 0.05$	210 ± 2.5	Nölle et al., 1999	(a,d,e)
$\Phi_1 + \Phi_3 = 0.85 \pm 0.25$	210		(a,b,e)
$\Phi_1 + \Phi_3 = 0.77 \pm 0.33$	222.5		(a,b,e)
$\Phi_1 + \Phi_3 = 0.71 \pm 0.30$	230		(a,b,e)
$\Phi_1 + \Phi_3 = 0.52 \pm 0.14$	248		(a,b,e)

Comments

(a) The measured quantum yield is for the loss of C(O)FCl. The observed products were $C(O)F_2$ (and in the study of Hermann et al. (1994), also CO). Product formation was explained using only channels (1) and (3), because decomposition of ClCO formed in channel (2) makes channel (2) equivalent to channel (3). Formation of $C(O)F_2$ arises from the self-reaction of FCO radicals formed in channel (1), FCO + FCO → $C(O)F_2$ + CO. Channel (3) should not be accessible for wavelengths >231 nm, and hence the quantum yield measured by Nölle et al. (1999) at 248 nm is expected to be that for channel (1).

(b) Laser photolysis at 298 K.

(c) The initial C(O)FCl pressure was in the range 7-11 mbar. In addition to experiments in the absence of diluent gas, experiments were carried out with added N_2 diluent gas at total pressures of 100 and 900 mbar. The relative contribution of channels (1) and (3) depended on pressure with an equal contribution of the two channels at 900 mbar N_2.

(d) Photolysis with a medium pressure mercury lamp-monochromator combination at 298 K.

(e) The initial C(O)FCl pressure was ~ 5 mbar, with no added diluent gas.

Preferred Values

Absorption cross-sections for C(O)FCl at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
186.0	15.6	207.3	10.8
187.8	14.0	209.4	9.9
189.6	13.4	211.6	9.0
191.4	12.9	213.9	7.9
193.2	12.7	216.2	6.9
195.1	12.5	218.6	5.8
197.0	12.4	221.0	4.8
199.0	12.3	223.5	3.8
201.0	12.5	226.0	2.9
203.0	12.0	228.6	2.2
205.1	11.5	231.2	1.6

Quantum yields for C(O)FCl photolysis at 298 K

See Comments on Preferred Values

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Chou et al. (1977) over the wavelength range 186 to 199 nm and those reported by Nölle et al. (1993) at longer wavelengths. The spectrum shows little structure; the values listed are averages over 500 cm^{-1} intervals. Nölle et al. (1993) reported values over the wavelength range 200-260 nm and the temperature range 298-223 K. Their room temperature values are in good agreement with those of Chou et al. (1977). The effect of temperature on calculated photodissociation rates is negligible because no strong temperature dependence is observed in the atmospheric window region where photolysis occurs (190-230 nm). Hermann et al. (1994) and Nölle et al. (1999) photolyzed C(O)FCl at a number of specific wavelengths in the range 193-248 nm. Within the substantial measurement uncertainties, the overall quantum yield for loss of C(O)FCl decreases approximately linearly with wavelength from 1.0 at 193 nm to 0.5 at 248 nm. Until confirmatory data are available, use of the quantum yields measured by Hermann et al. (1994) and Nölle et al. (1999) is recommended. Pulsed laser photolysis at 235 nm of C(O)FCl in a supersonic jet coupled to time-of-flight spectroscopy showed that channel (1) is operative at this wavelength (Maul et al., 1999), and a value of ΔH^o(C(O)FCl)[0 K] = –(397 ± 15) kJ mol^{-1} was obtained.

References

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Maul, C., Dietrich, C., Haas, T. and Gericke, K.-H.: Phys. Chem. Chem. Phys., 1, 1441, 1999.
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