IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PCl4

This data sheet updated: 5th June 2007.

$Cl_2O + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$Cl_2O + h\nu \rightarrow Cl + ClO$	(1)	142	840
$\rightarrow O + Cl_2$	(2)	168	710
$\rightarrow O + 2Cl$	(3)	410	292

Preferred Values

Absorption cross-sections for Cl_2O at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	69.0	305	53.2	410	1.09
205	43.5	310	39.3	415	1.18
210	23.6	315	27.8	420	1.23
215	12.8	320	19.0	425	1.23
220	8.95	325	12.9	430	1.21
225	12.7	330	8.70	435	1.15
230	28.2	335	6.06	440	1.09
235	57.6	340	3.86	445	0.959
240	101	345	2.61	450	0.842
245	150	350	1.77	455	0.730
250	187	355	1.28	460	0.623
255	199	360	0.862	465	0.531
260	189	365	0.614	470	0.451
265	168	370	0.478	475	0.377
270	147	375	0.444	480	0.312
275	133	380	0.453	485	0.277
280	123	385	0.506	490	0.251
285	113	390	0.587	495	0.231
290	101	395	0.706	500	0.216
295	85.6	400	0.832		
300	69.2	405	0.968		

Quantum Yields

$\phi(1) = 1.0$ at $\lambda > 300$nm; $\lambda < 300$ nm see comments

Comments on Preferred Values

The preferred values of the absorption cross-sections between 200 and 500 nm at 298 K are an average of the datasets of Knauth et al. (1979) (200-500 nm) and Lin (1976), (180-640 nm). The preferred values are in excellent agreement with those reported by Molina and Molina (1978), which extend to 450 nm. They are also in good agreement with the values reported by Johnsson et al. (1995) ($\sigma = 186\times10^{-20}$ cm^2 at 260 nm) and by Lin (1976) ($\sigma = 183\times10^{-20}$ cm^2 at 260 nm). Values for the 150-200 nm wavelength region have been reported by Nee (1991).

Photolysis proceeds predominantly by breaking of the Cl-O bond to yield Cl + ClO. However, Sander and Friedl (1989) determined the quantum yield for formation of oxygen atoms from Cl_2O photolysis to be 0.25 ± 0.05, the main products being Cl+ClO. In these experiments a broad-band photolysis source with a spectral distribution extending from the visible down to 180 nm was used, so that it was not possible to determine the wavelength dependence of the quantum yield. Nelson et al. (1994) used photofragment translational energy spectroscopy in a molecular beam to study the photodecomposition of Cl_2O at 308, 248 and 193 nm. In all cases reaction (1) occurs. At 308 nm the only channel is Cl + ClO; this is the major channel at 248 nm and a minor channel at 193 nm. At 248 nm the ClO fragment dissociates spontaneously. At 193 nm a concerted dissociation pathway leads to the formation of O + Cl_2. Almost all of the primary Cl_2 photoproducts dissociate. Nickolaisen et al. (1996) have studied the pressure dependence of Cl_2O photodissociation. The observed pressure dependence of ClO formation was explained assuming that, after Cl_2O excitation at $\lambda > 300$ nm, a rapid intersystem crossing between two metastable states operates. These states were assumed to undergo competitive dissociation to Cl + ClO and collisional relaxation to the ground state. However, this interpretation appears to be in disagreement with lifetime estimates by Moore et al. (1997). A detailed investigation of the dynamics of the complicated photodissociation process using the photoimaging technique was reported by Tanaka et al. (1998).

References

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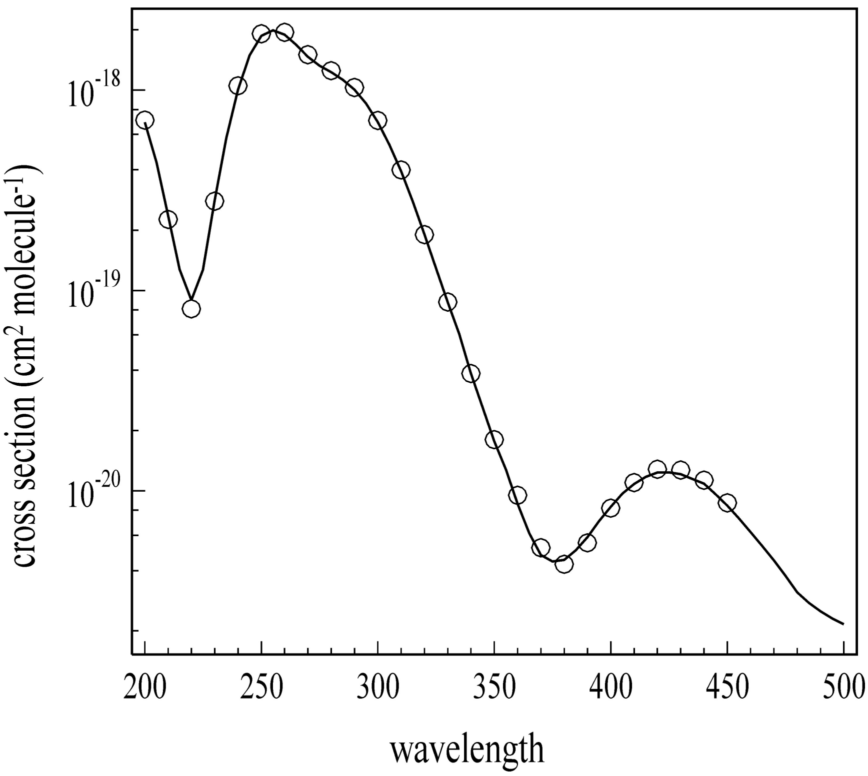

Cl_2O absorption spectrum: Preferred value (solid line, see text for details) and comparison with Molina and Molina, 1978 (circles).