IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II PCl5

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This data sheet last evaluated: June 2011; last change in preferred values: June 2011.

Cl_2O_2 + hν → products

Primary photochemical processes

Reaction		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
Cl_2O_2 + hν → ClO + ClO	(1)	76	1580
→ Cl + ClOO	(2)	91	1310
→ Cl + ClO + O(^{3}P)	(3)	344	349

Preferred Values

Absorption cross-sections for ClOOCl (190 - 250 K)

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	423	256	549	312	38.2	368	5.23
202	395	258	495	314	35.3	370	4.77
204	362	260	445	316	32.8	372	4.35
206	331	262	400	318	30.4	374	3.95
208	303	264	360	320	28.2	376	3.60
210	277	266	325	322	26.3	378	3.27
212	255	268	294	324	24.7	380	2.97
214	238	270	268	326	32.2	382	2.70
216	228	272	246	328	21.9	384	2.45
218	225	274	225	330	20.7	386	2.24
220	232	276	206	332	19.5	388	2.04
222	249	278	189	334	18.4	390	1.87
224	277	280	173	336	17.3	392	1.71
226	316	282	158	338	16.3	394	1.58
228	366	284	144	340	15.4	396	1.47
230	424	286	131	342	14.5	398	1.36
232	488	288	119	344	13.6	400	1.26
234	555	290	108	346	12.7	402	1.18
236	618	292	98.2	348	11.9	404	1.11
238	674	294	88.9	350	11.1	406	1.05
240	719	296	80.5	352	10.3	408	0.988

242	747	298	72.9	354	9.55	410	0.933
244	758	300	66.1	356	8.82	412	0.878
246	753	302	59.9	358	8.10	414	0.831
248	732	304	54.4	360	7.43	416	0.778
250	697	306	49.7	362	6.81	418	0.738
252	651	308	45.4	364	6.24	420	0.712
254	601	310	41.6	366	5.72	>420	a

[a]At $\lambda > 420$ nm the NASA-JPL panel (Sander et al., 2011) recommend use of $\sigma(\lambda) = 9.5 \times 10^{-16} \exp(-0.0281\lambda)$ with λ in nm and σ in cm^2 $molecule^{-1}$.

Quantum yields for Cl_2O_2 photolysis

$\phi_1 = 0.1 \pm 0.1$ throughout the range 200-400 nm.
$\phi_2 = 0.9 \pm 0.1$ throughout the range 200-400 nm.

Comments on Preferred Values

Absolute values for ClOOCl absorption cross sections have been determined by Cox and Hayman (1988), Burkholder et al. (1990), DeMore and Tschuikow-Roux (1990), Bloss et al. (2001) and Papanastasiou et al. (2010) by applying chlorine balance within a chemical system in which ClOOCl was generated photochemically. Relative spectra, converted to absolute values by normalisation at λ_{max}, have been published by Huder and Demore (1995) and Pope et al. (2008). A spectrum of matrix isolated ClOOCl (10 K, Ne matrix) is also available (von Hobe et al., 2009). Older spectra, (Basco and Hunt, 1979; Molina and Molina, 1987) were later shown to be heavily contaminated with other absorbers such as Cl_2O_3.

Whereas the spectra show reasonable agreement at wavelengths close to the maximum ($\approx$ 245 nm) there are significant differences in cross sections at longer wavelengths, which are related to spectral subtraction of e.g. Cl_2O, Cl_2 and Cl_2O_3. Spectral subtraction of Cl_2, which is always present as impurity, is particularly difficult as ClOOCl appears to have a spectral feature which is very similar to the Cl_2 spectrum and this is thought to have lead to the very low cross sections reported by Pope et al (2008). at wavelengths longer that ~290 nm.

This problem has been overcome by either a) taking into account all absorbers using a multiple isosbestic point analysis (Papanastasiou et al., 2009), b) by determining the photodissociation cross section via relative loss of ClOOCl and a reference molecule gas with known cross section and quantum yield (Chen et al., 2009 (308, 351 nm) ; Lien et al., 2009 (248 nm) and Jin et al., 2009 (330 nm)) or c) by measuring a photodissociation cross section for Cl atom formation (at 248, 308 and 352 nm) with correction for Cl_2 impurity (Wilmouth et al., 2009). The absorption cross sections reported by Chen et al., (2009), Lien et al., (2009), Jin et al., (2009) and Wilmouth et al., (2009) were all calculated assuming a photodissociation quantum yield of unity are therefore lower limits. In the case of Wilmouth et al. (2009) it is also assumed that two Cl atoms are formed (see text below on quantum yields). The cross sections reported by these methods are in good agreement and show little or no temperature dependence over the atmospheric range. Our preferred values are thus those reported by (Papanastasiou et al., 2009).

Pulsed photolysis at isolated laser wavelengths have shown that channel (2) dominates with Cl atoms formed with near unity quantum yield, which agrees with the interpretation of the steady-state photolysis experiments of Cox and Hayman (1988). The direct results are summarised in the Table below.

	248 –250 nm		308 nm	
ϕ_1 $ClOOCl \rightarrow 2\ ClO$	0.12 ± 0.07 < 0.02	(Moore et al., 1999) (Plenge et al., 2004)	0.1 ± 0.1 <0.1	(Moore et al., 1999) (Plenge et al., 2004)

	0.08 (Huang et al., 2011)	0.19 (Huang et al., 2011)
ϕ_2 $ClOOCl \rightarrow 2\ Cl + O_2$	0.88 ± 0.07 (Moore et al., 1999) >0.98 (Plenge et al., 2004) 0.82 (Huang et al., 2011)	1.03 ± 0.12 (Molina et al., 1990) 0.9 ± 0.1 (Moore et al., 1999) >0.9 (Plenge et al., 2004) 0.81 (Huang et al., 2011)
ϕ_3 $ClOOCl \rightarrow ClO + Cl + O$	0.1 (Huang et al., 2011)	

methods:

Molina et al.: Resonance fluorescence, Plenge et al.: Photoionisation mass spectrometry, Moore et al., Huang et al.: Photofragment translational spectroscopy.

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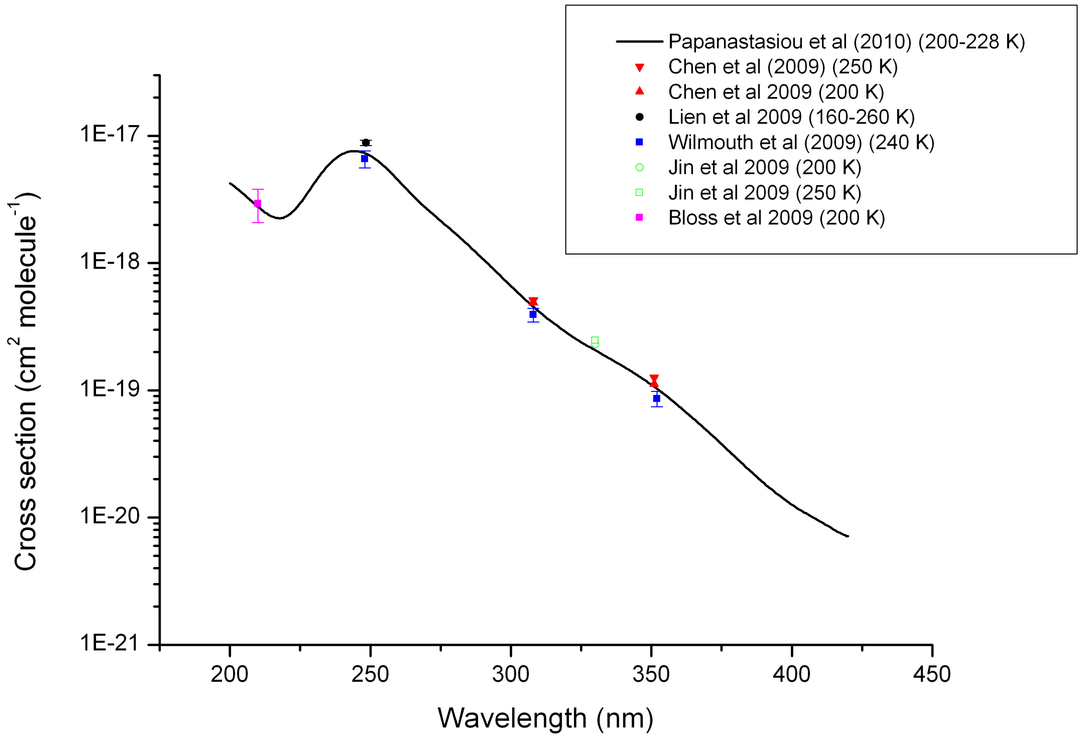
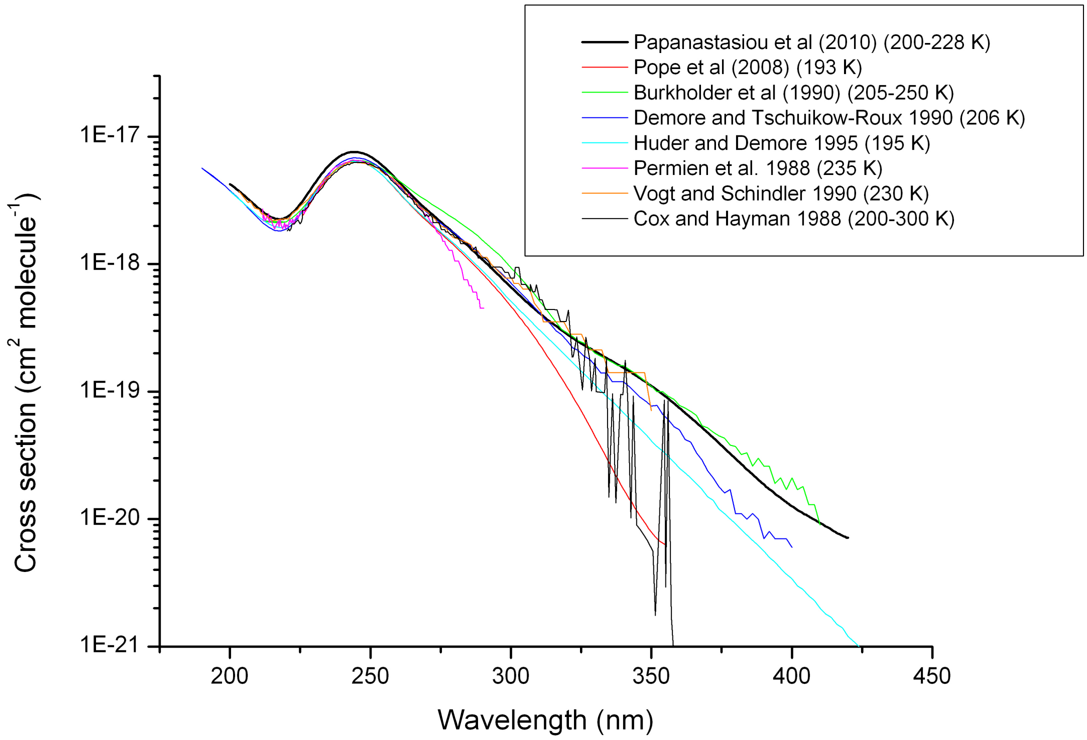


Absorption cross sections of ClOOCl. the solid black line (Papanastasiou et al. 2009) are preferred values.



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