IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet III.A5.110 PCl9

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$ClNO_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$ClNO_2 + h\nu \rightarrow Cl + NO_2$	(1)	142	843
$\rightarrow ClNO + O(^3P)$	(2)	288	415

Preferred Values

Absorption cross-sections (σ) for $ClNO_2$ at 296 K

λ (nm)	σ (10^{-20} cm^2)	A_1 (λ)	A_2 (λ)	λ (nm)	σ (10^{-20} cm^2)	A_1 (λ)	A_2 (λ)
205	309.8	211	1.85	340	3.572	397.9	0.86
210	326.2	96	1.50	345	2.734	459.8	0.97
215	346.2	68	1.38	350	2.077	522.1	1.14493
220	325.7	73	1.29	355	1.564	593	1.46169
225	282.7	105	1.26	360	1.170	660.3	1.71663
230	222.3	155	1.29	365	0.8726	726.4	2.00104
235	171.2	203	1.36	370	0.6501	792.1	2.33777
240	135.7	229	1.39	375	0.4836	850.9	2.60668
245	111.5	242	1.48	380	0.3593	910.8	2.92818
250	92.86	239	1.50	385	0.2687	974	3.34597
255	76.12	230	1.44	390	0.2008	1024.7	3.65781
260	60.26	246	1.54	395	0.1498	1080.8	3.97039
265	46.26	268	1.69	400	0.1125	1143.2	4.4706
270	35.11	258	1.65	405	0.08471	1174.7	4.52843
275	27.12	236	1.58	410	0.06419	1236	5.16769
280	22.50	194	1.52	415	0.04858	1231.6	4.89102
285	18.80	136	1.36	420	0.03627	1257	4.91924
290	17.05	84	1.17	425	0.02777	1411.4	7.03785
295	15.85	60	1.04	430	0.02168	1332.4	5.69311
300	14.75	58	0.91	435	0.01668	1528.6	8.564
305	13.48	73	0.82	440	0.01234	1161.9	2.753
310	12.03	99	0.74	445	0.009395	1410	6.785
315	10.42	135.6	0.70	450	0.007482	1550.1	8.966
320	8.809	176.8	0.66	455	0.006059	1357.1	5.061
325	7.246	227.6	0.69	460	0.004981	2100.9	17.81
330	5.831	278.8	0.68	465	0.003794	2395.2	21.91
335	4.600	336.4	0.74	470	0.003169	1401.8	6.412

The cross sections listed are 5 nm averages centred around the listed wavelength. Temperature dependent values of σ may be calculated from the following expression using the A_1 and A_2 parameters listed in table above (Ghosh et al.2012):

$$\sigma(\lambda,T) = \sigma(\lambda, 296\ K) \times (1 + 10^{-5}A_1(\lambda) \times (T-296) + 10^{-5}A_2(\lambda) \times (T-296)^2)$$

Quantum yield for $ClNO_2$ photolysis

$\phi_1 = 1.0$ for $\lambda > 300$ nm

Comments on Preferred Values

The preferred values of the absorption cross-sections are the values reported by Ghosh et al (2012) which cover the largest and atmospherically most relevant wavelength range and also provide information on the temperature dependence. Note that a relative absorption spectrum was obtained and normalized to a value of 3.481×10^{-18} cm^2 molecule^{-1} at 216 nm. The room temperature cross sections presented by Ghosh et al (2012) are in excellent agreement with the values reported by Martin and Gareis (1956), Ganske et al (1992) and Nelson and Johnston (1981). Weak and diffuse vibrational structure is superimposed on the continuum between ≈ 220 and 280 nm (Miller and Johnson 1993; Furlan et al., 2000; Ghosh et al., 2012).

At wavelengths of > 300 nm, photodissociation to form Cl and NO_2 occurs with a quantum yield of close to unity. Nelson and Johnston (1981) derived a quantum yield of $\phi_1 = 0.93 \pm 0.15$ at 350 nm and found no evidence for O(^{3}P) production ($\phi_2 < 0.02$). However, at increasing photon energies O(^{3}P) is detected in increasing yields. At 308 nm Plenge et al. derived $\phi_1 = 0.93$ and $\phi_2 = 0.07$ whilst at 248 nm or 240 values of $\phi_2 = 0.15 \pm 0.03$ (Ghosh et al. 2012) or 0.5 (Plenge et al 2001) have been reported. The result of Furlan et al (2000) who found no evidence for O(^{3}P) generation at 248 nm is not consistent with this, which may indicate differences between thermal experiments in bath gas or in rotationally cold molecular beams. Furlan observed O-atoms only at high laser fluences and attributed this to secondary dissociation of NO_2 from channel 1. At 193 nm O(^{3}P) is the dominant product detected with a yield of 0.67 ± 0.12 (Ghosh et al. 2012). At 235 and 248 nm, the product NO_2 from reaction (1) is formed both in the electronic ground state and in excited electronic states (Miller and Johnston, 1993; Carter et al., 1999; Furlan et al., 2000) and some of the O(^{3}P) formed at shorter wavelengths may be attributable to prompt dissociation of excited NO_2 formed in channel 1.

Whilst recognising that some direct O(^{3}P) formation is possible at the shortest wavelengths available in the lower atmosphere (> 300 nm), for the purpose of modelling $ClNO_2$ dissociation in this region we suggest use of a quantum yield of unity for channel 1. The impact of a small branching ratio of channel 2 (to O(^{3}P) and ClNO) or the prompt dissociation of NO_2 formed in channel 1 to O(^{3}P) will be slight as the fate of both ClNO and NO_2 is in any case largely dominated by photodissociation to form the same products.

References

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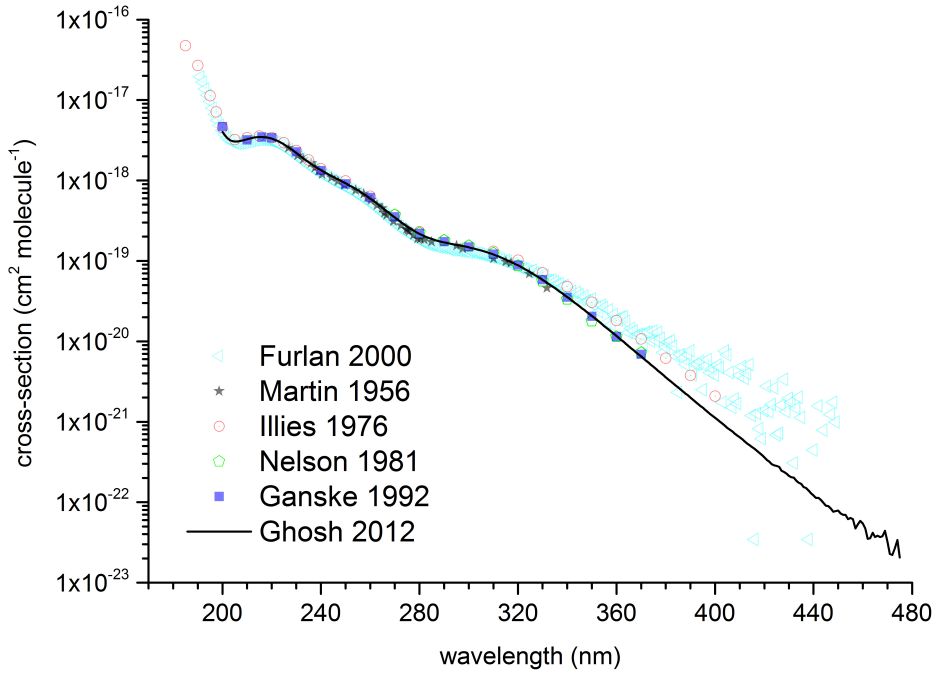

Absorption cross sections of $ClNO_2$ at room temperature: The solid line (data of Ghosh et al. 2012) represents the preferred values.