IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PCl10

This data sheet updated: 20th July 2006.

$ClONO_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction			$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$ClONO_2 + h\nu$	$\rightarrow ClO + NO_2$	(1)	112	1065
	$\rightarrow Cl + NO_3$	(2)	163	735
	$\rightarrow ClONO + O(^3P)$	(3)	282	425

Preferred Values

Absorption cross-sections for $ClONO_2$ at 296 and 220 K

λ/nm	10^{20} σ/cm^2		λ/nm	10^{20} σ/cm^2	
	296 K	220 K		296 K	220 K
200	282	270	315	1.14	
205	284		320	0.831	0.578
210	314	315	325	0.613	
215	342		330	0.466	0.329
220	332	335	335	0.367	
225	278		340	0.302	0.230
230	208	200	345	0.258	
235	148		350	0.229	0.186
240	105	96.7	355	0.208	
245	76.4		360	0.200	0.169
250	56.0	49.7	365	0.180	
255	43.2		370	0.159	0.136
260	33.8	29.1	375	0.141	
265	26.5		380	0.121	0.104
270	20.5	17.3	385	0.137	
275	15.7		390	0.091	0.077
280	11.9	9.83	395	0.076	
285	8.80		400	0.064	0.052
290	6.41	5.15	405	0.054	
295	4.38		410	0.044	0.034
300	3.13	2.40	415	0.036	
305	2.24		420	0.032	0.023
310	1.60	1.16	425	0.023	
			430	0.019	0.013

Quantum yields for $ClONO_2$ photolysis

$\phi_2(\lambda < 308\ nm) = 0.6$
$\phi_2(\lambda\ 308\text{-}364\ nm) = 7.143 \times 10^{-3}\ \lambda\ (nm) - 1.60$
$\phi_2(\lambda > 364\ nm) = 1.0$

$\phi_1(\lambda) = 1 - \phi_2(\lambda)$.

Comments on Preferred Values

The preferred values of the absorption cross-sections are taken from Burkholder et al. (1994), whose measurements covered the wavelength range 195-430 nm and the temperature range 220-296 K. They report (Burkholder et al., 1994), every 2 nm, values of σ at 296 K and values of the parameters A_1 and A_2 needed to compute the temperature dependence by the equation:

$$\sigma(\lambda,T)/\sigma(\lambda,196) = 1 + A_1(T-296)+A_2(T-296)^2$$

In this data sheet, room temperature values at 5 nm intervals and values for 220 K at 10 nm intervals are given. These values are in good agreement with the results of Molina and Molina (1979).

Photolysis quantum yields have been derived by observation of the radical fragments, Cl, ClO, NO_3 and $O(^3P)$. The most recent studies (Ravishankara, 1995; Moore et al., 1995; Nelson et al., 1996; Nickolaisen et al., 1996; Tyndall et al., 1997; Goldfarb et al., 1997; Yokelsen et al., 1997; Zou et al., 2002) approach a general agreement of the wavelength dependence of the quantum yields ϕ_1, ϕ_2, and ϕ_3, and are considered more reliable than older investigations (Margitan, 1983; Knauth and Schindler, 1983; Chang et al., 1979). Despite generally good agreement, some discrepancies, in particular pressure dependences, such as observed in Nickolaisen et al. (1997) were not reproduced in Tyndall et al. (1997), Goldfarb et al. (1997) and Yokelsen et al. (1997) and remain unexplained. The preferred values are based on the results of Goldfarb et al. (1997) and Yokelsen et al. (1997), who have the most extensive dataset. The results obtained are ϕ_1 = 0.60, 0.40, and 0.35 for λ = 222, 248, and 308 nm respectively. ϕ_2 = 0.40, 0.60, 0.65, and 0.93 for λ = 222, 248, 308, and 352.5 nm, respectively. Oxygen atoms have been observed in several experiments, though they cannot be unambiguously assigned to channel (3) as some (or all) are formed by the decomposition of hot NO_3 radicals formed when $ClONO_2$ is photolysed at short wavelengths, e.g. Zou et al. (2002).

The preferred quantum yields follow recommendations of the JPL-NASA evaluation panel (Sander et al., 2006). There appears to be no significant change in ϕ_2 between 248 and 308 nm so that a wavelength independent quantum yield of 0.6 is appropriate. ϕ_2 increases with wavelength at the expense of ϕ_1 between 308 and 364 nm, so that a wavelength dependence is given. Above 364 nm ϕ_2 is close to unity, so that ϕ_1 becomes zero.

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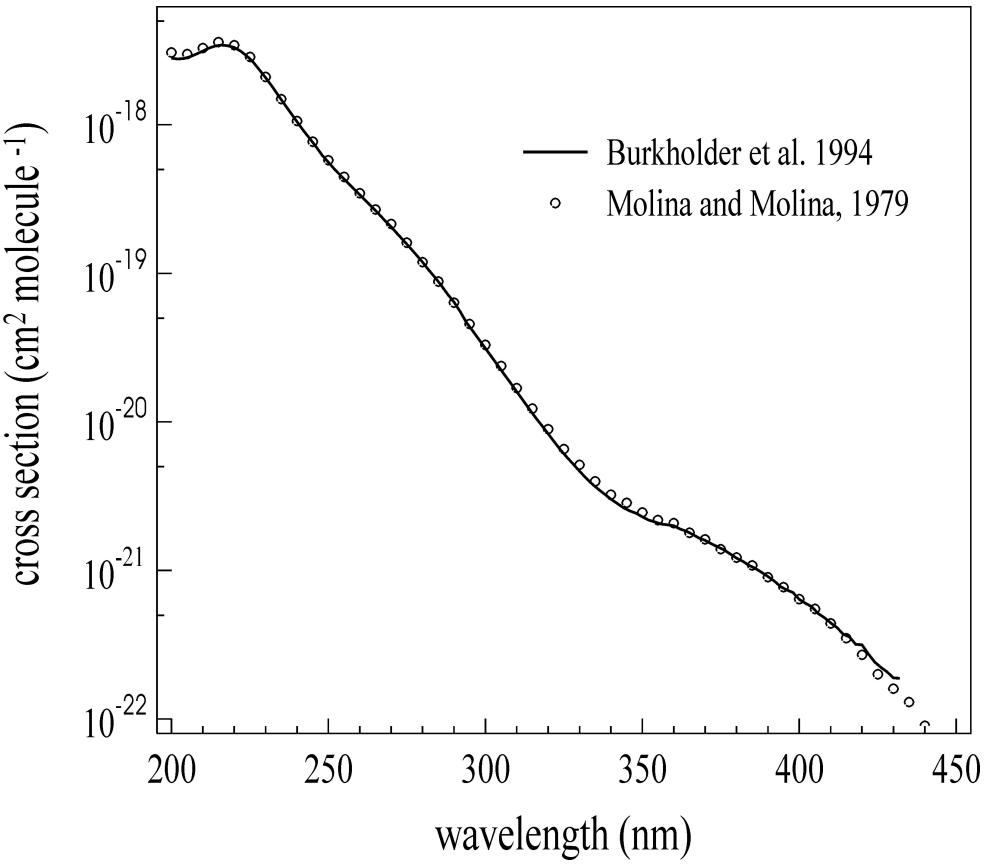

Absorption cross sections of $ClONO_2$: The solid line (Burkholder et al., 1994) represents the preferred values at 296 K.