IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PI5

This data sheet updated: 15th December 2000.

ICl + hν → products

Primary Photochemical Transitions

Reaction	$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
ICl + hν → I + Cl	211	567
→ Cl($^2P_{1/2}$) + I	221	540
→ Cl + I($^2P_{1/2}$)	302	396

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220-600	Seery and Britton, 1964[1]	(a)
210-530	Jenkin et al., 1990[2]	(b)

Quantum yield data

Wavelength/nm	Quantum yield	Reference	Comments
235.3-237.8	$\Phi(Cl^*) = 0.40$	Tonokura et al., 1993[3]	(c)
248	$\Phi(I^*) = 0.42$		

Comments

(a) Three measurements of the UV/Vis absorption spectrum have been performed in a 10 cm long quartz cell and the pressure was measured using a Pyrex spiral manometer. Runs with added Cl_2 indicated the disproportionation reaction to be immeasurably slow under the prevailing experimental conditions. The uncertainty in the absorption cross section was ± 0.2x10^{-20} throughout the wavelength range.

(b) Spectrum of a static purified gas sample of ICl using a CCD camera over the wavelength range 210-690 nm. Good agreement with the spectrum of ref. 1 except in the range 290-360 nm where the measured values of the cross sections seem to be lower than in ref. 1 presumably owing to a

Cl$_2$ impurity. The value of the UV maximum $\sigma = 5\times10^{-19}$ cm^2 molecule^{-1} at 240 nm is slightly higher than in ref. 1 by approximately 5-10%.

(c) The stated relative quantum yields are consistent with the following measured concentration ratios observed in the diffusive molecular beam photodissociation experiment with REMPI detection of [Cl*] and [Cl] and two-photon laser-induced fluorescence of [I] and [I*], respectively : [Cl*]/[Cl] = 0.68 ± 0.10 in the range 235.3-237.8 nm and [I*]/[I] = 0.71 ± 0.27 at 248 nm. By inference the quantum yield for the ground state process is 0.18.

Preferred Values

Absorption Cross Sections at 298K

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2
220	21.33	420	28.87
230	35.36	430	32.08
240	43.97	440	35.44
250	43.32	450	38.85
260	35.25	460	41.67
270	24.35	470	42.59
280	15.41	480	40.91
290	9.41	490	36.32
300	6.08	500	29.44
310	4.59	510	22.79
320	4.01	520	16.40
330	3.67	530	11.47
340	3.29	540	8.00
350	3.10	550	5.70
360	3.52	560	4.32
370	5.31	570	3.44
380	8.79	580	2.83
390	13.88	590	2.10
400	18.96	600	1.76
410	24.66		

Comments on Preferred Values

The listed cross sections are the only ones available.

References

[1] D. Seery and D. Britton, J. Phys. Chem. **68**, 2263 (1964).
[2] M. E. Jenkin,R. A. Cox, A. Mellouki, G. LeBras, and G. Poulet, J. Phys. Chem. **94**, 2927 (1990).
[3] K. Tonokura,Y. Matsumi, M. Kawasaki, H. L. Kim, Sh. Fujimura, and K. Saito, J. Chem. Phys. **99**, 3461 (1993).