IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PI3

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IO + hυ → products

Primary photochemical processes

Reaction		$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
IO+ hν → I + O(^{3}P)	(1)	240	500
→ IO + O(^{1}D)	(2)	430	280

Absorption cross-section data

Wavelength range/nm	Reference	Comments
427.2	Sander, 1986[1]	(a)
340-450	Laszlo, Kurylo, and Huie, 1995[2]	(b)
340-480	Harwood *et al.*, 1997[3]	(c)
345-465	Atkinson, Hudgens, and Orr-Ewing, 1999[4]	(e)
345-465	Bloss et al., 2001[5]	(d)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 > 0.90 \pm ^{0.19}_{0.26}$	355	Ingham *et al.*, 2000[6]	(f)

Comments

(a) Flash photolysis-absorption spectroscopy study. Cross-sections at the head of the 4-0 band at 427.2 nm were measured at six temperatures in the range 250 K to 373 K. A strong temperature dependence was observed at temperatures <315 K, with σ increasing with decreasing temperature.

(b) Pulsed laser photolysis-absorption spectroscopy study. A cross-section of σ(427.2 nm) = (2.8 ± 0.5) x 10^{-17} cm^2 molecule^{-1} at 298 K was obtained, at a resolution of 0.3 nm.

(c) Pulsed laser photolysis-absorption spectroscopy study. Cross-sections of σ(427.2 nm) = (3.0 ± 0.4) x 10^{-17} cm^2 molecule^{-1} and (3.6 ± 0.5) x 10^{-17} cm^2 molecule^{-1} were reported for resolutions of 0.44 nm and 0.14 nm, respectively, at 298 K.

(d) Pulsed laser photolysis of N_2O-CF_3I mixtures. IO radicals were detected by time-resolved CCD measurements of the post-laser pulse mixtures in the range 340 nm to 470 nm. Cross-sections of σ(427.2 nm) = (1.9 ± 0.2) x 10^{-17} cm^2 molecule^{-1} (resolution of 1.13 nm) and σ(395.5 nm) = (5.7

± 0.5) x 10^{-18} cm^2 $molecule^{-1}$ were reported. They also reported a small temperature dependence of the cross-section at 427.2 nm, based on an analysis of the differential cross-section and taking into account the temperature and pressure dependence of the yield of IO radicals from the $O(^3P) + CF_3I$ reaction.

(e) Pulsed laser photolysis of N_2O-CF_3I mixtures. IO radicals were detected by time-resolved cavity ring-down spectroscopy (CRDS) at 445.40 nm (band head of rotationally resolved 2-0 band) and 455 nm (maximum of the diffuse 1-0) band). Cross-sections of σ(445.40 nm) = (7.3 ± 0.7) x 10^{-17} cm^2 $molecule^{-1}$ and σ(455 nm) = (7.3 ± 0.8) x 10^{-18} cm^2 $molecule^{-1}$ were obtained using absolute value of 1.05 x 10^{-17} cm^2 $molecule^{-1}$ at 298 K obtained by Laslo *et al*[2] for the 2-0 band head at a resolution of 0.3 nm.

(f) Pulsed laser photolysis (248 nm) of O_3-I_2 mixtures, with photolysis of IO radicals by second laser pulse at 355 nm after a fixed time delay. $O(^3P_j)$ detected by time-resolved RF. Quantum yield measured relative to NO_2 photolysis at the same wavelength.

Preferred Values

Absorption cross-sections for IO at 298 K

λ/nm	10^{18} σ/cm^2	λ/nm	10^{18} σ/cm^2
345	0.78	410	7.53
350	1.00	415	5.18
355	1.36	420	9.04
360	1.85	425	4.17
365	2.25	430	6.11
370	2.99	435	6.92
375	3.57	440	1.61
380	4.42	445	4.94
385	4.63	450	1.02
390	5.65	455	2.36
395	6.55	460	0.90
400	6.40	465	0.39
405	7.09		

Quantum Yields

$\phi(1) = 1.0$ throughout the wavelength range 345 – 465 nm.

Comments on Preferred Values

Absorption Cross-Sections. The measurements of the cross-sections at the band head of the 4-0 band at 427.2 nm by Laszlo *et al*.,[2] Harwood *et al*.[3] , Bloss *et al*.[5] are in fairly good agreement when the effects of resolution are taken into account. These data[2-4] suggest a slightly higher value than the earlier data of Sander,[1] Stickel *et al*.[7] and Cox and Coker[8] . We recommend a value of σ(427.2 nm) = 3.6±0.3 x 10^{-17} cm^2 $molecule^{-1}$ based on the measurements of Harwood *et al.* [2] for the 4-0 band at high resolution (0.14 nm). The information from the studies of Harwood *et al*.[3] and also of Hudgens *et al*[4] at 298 K on the IO band shape and cross section at high resolution can be used to calculate the expected intensity and shape of the bands at lower resolution, which shows that the recent studies are consistent with this recommendation.

The study of Laszlo *et al*.[2] showed that the vibronic band structure is superimposed on a broad continuous absorption which maximizes at ~400 nm. Other recent studies[3,5] confirm the presence of the underlying continuum, which makes a significant contribution to atmospheric photolysis.

Bloss *et al.*[5] showed that IO absorption measurements in the 340 nm to 450 nm region can be influenced by the presence of an underlying absorption due to a product of the IO + IO reaction, and this was accounted for in their reported values for σ in the continuum region[5]. However Harwood *et al.* [2] observed the same decay kinetics when IO was monitored in the continuum region at 390 nm suggesting no interference due to product absorption. The agreement is good in thereported overall shape of the IO absorption envelope in the continuum between 350-400 nm where resolution is unimportant, from the three studies. The absolute cross sections reported by Bloss *et al*.[5] in the continuum at 390 nm are a factor of 0.67 lower than those from Laszlo *et al*,[2] and Harwood *et al*,[3]. The preferred values for the IO cross-sections averaged over 5 nm intervals in the 345 nm to 465 nm are the values given by Bloss *et al*.[5], scaled upwards by a factor of 1.5 to compensate for the lower resolution-independent value of σ(390 nm), obtained in this study.
The temperature dependence of σ(427.2 nm) has been investigated by Sander,[1] Harwood *et al*.[3] and Bloss *et al*.[5]. The studies of Harwood *et al*.[3] and Bloss *et al*.[5] did not reproduce the large increase in σ with decreasing temperature below 315 K observed by Sander,[1] although values of σ above 315 K are in good agreement.[1,3,5] Bloss *et al*.[5] found that the yield of IO from the $O(^3P) + CF_3I$ reaction is apparently pressure and temperature dependent, and this was accounted for in deriving their expression for the small temperature dependence of σ(427.2 nm). Harwood *et al*.[3] assumed a constant yield of IO from the $O(^3P) + CF_3I$ reaction which resulted in a temperature-independent cross-section σ at 427.2 nm. Since the temperature dependence is clearly quite small, cross-sections in the banded region at low resolution can be assumed to be temperature independent. Cross sections in the continuum region are assumed to be temperature and resolution independent.

Quantum Yields. Turnipseed *et al*.[9] observed LIF from the (0,0), (2,0), (3,0) and (2,1) bands of the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ transition of IO. The spectra are predissociated and the dissociation lifetime is <10 ns.[10] The lifetime of the upper state of IO formed in the A-X transition is thus so short that quenching, fluorescence and processes other than dissociation by reaction (1) must be negligible, and therefore the predominant fate of IO following light absorption is dissociation to O + I. The measurement of Ingham *et al*.[6] in the continuum at 355 nm confirms this conclusion for that region.

References

1 S. P. Sander, J. Phys. Chem. **90**, 2194 (1986).
2 B. Laszlo, M. J. Kurylo and R. E. Huie, J. Phys. Chem. **99**, 11701 (1995).
3 M. H. Harwood, J. B. Burkholder, M. Hunter, R. W. Fox, and A. R. Ravishankara, J. Phys. Chem. A **101**, 853 (1997).
4 D . B. Atkinson, J. W. Hudgens, and A. J. Orr-Ewing, J. Phys. Chem. A **103**, 6173 (1999).
5 W .J. Bloss, D.M. Rowley, R.A. Cox, and R.L. Jones, J.Phys.Chem. A, **105**, 7885, (2001).
6 T. Ingham, M. Cameron amd J.N. Crowley, J.Phys.Chem.A, **104**, 8001, (2000)
7 R. E. Stickel, A. J. Hynes, J. D. Bradshaw, W. L. Chameides, and D. D. Davis, J. Phys. Chem. **92**, 1862 (1988).
8 R. A. Cox and G. B. Coker, J. Phys. Chem. **87**, 4478 (1983).
9 A. A. Turnipseed, M. K. Gilles, J. B. Burkholder, and A. R. Ravishankara, Chem. Phys. Lett. **242**, 427 (1995).
10 G. Inoue, M. Suzuki, and N. Washida, J. Chem. Phys. **79**, 4730 (1983).