

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PI4

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OIO + hv → products

Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
OIO+ hv → I + O ₂	(1)	30	3987
→ IO + O(³ P)	(2)	288	415

Absorption cross-section data

Wavelength range/nm	Reference	Comments
465-667	Himmelman <i>et al.</i> , 1996 ¹	(a)
549.1	Spietz <i>et al.</i> , 1998 ²	(b)
548.6	Cox <i>et al.</i> , 1999 ³	(c)
548.6	Ingham, Cameron, and Crowley, 2000 ⁴	(d)
540-605	Ashworth, Allen and Plane, 2002 ⁵	(e)

Quantum yield data ($\Phi = \Phi_1 + \Phi_2$)

Measurement	Wavelength/nm	Reference	Comments
$\Phi_1 < 0.15$ $\Phi_2 < 0.007$	532	Ingham, Cameron, and Crowley, 2000 ⁴	(f)

Comments

- Flash photolysis of a mixture of I₂ in O₃ with time-resolved UV-visible absorption spectroscopy. In addition to IO bands between 21500 cm⁻¹ and 26000 cm⁻¹ (385 nm to 465 nm), a new absorption spectrum between 15000 cm⁻¹ and 21500 cm⁻¹ (465 nm to 667 nm) was observed, which was attributed to the OIO radical by comparison of the derived spectroscopic constants with the known values for OCIO and OBrO.
- Same technique as in comment (a). Fits to a complex mechanism yielded an estimate for $\sigma(\text{OIO}) = (3.5 \pm 1.5) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 549.1 nm.
- Pulsed laser photolysis of N₂O/Br₂/CF₃I mixtures at 193 nm with time-resolved UV-visible absorption spectroscopy using a charged-coupled-device detection system. The branching ratio for OIO formation in the IO self-reaction was determined to be 0.38 ± 0.08 . This is based on an

analysis assuming a branching ratio for OIO formation in the IO + BrO reaction of 0.8, as reported by Bedjanian *et al.*⁶ from a DF study in which the co-product Br was measured. A corresponding absolute value of $\sigma(\text{OIO}) = (1.09 \pm 0.21) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 548.6 nm was derived. Absorption bands were observed from 495 nm to 600 nm.

- (d) Pulsed laser photolysis of a mixture of O₃ in I₂ with UV-visible absorption spectroscopy and resonance fluorescence detection. A conservative minimum OIO cross section of $2.7 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 548.6 nm was derived. Absorption bands were observed from 480 nm to 650 nm.
- (e) Pulsed laser photolysis-CRDS/UVS; both high resolution and broadband spectra reported. The high resolution spectrum shows no fine structure in the bands which are attributed to the OIO(²B₂-²B₁) transition.
- (f) Same experimental conditions as in comment (d). Photofragment spectroscopy was used to study the quantum yield for O(³P) production and for I(²P_J) production following the photolysis of OIO at 532 nm. O(³P) was not detected, allowing the authors to put an upper limit of ~0.007 on the value of Φ_2 at 532 nm. I(²P_J) could not be detected in the single photon photolysis of OIO at 532 nm, and an upper limit of ~0.15 on the value of Φ_1 was derived.

Preferred Values

Absorption cross-sections

$$\sigma(\text{OIO}) = (2.7 \pm 1.6) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1} \text{ at } \lambda = 548.6 \text{ nm}$$

Quantum yields

$$\Phi_2 < 0.007 \text{ at } 532 \text{ nm}$$

Comments on Preferred Values

The absorption spectrum of OIO in the strong visible absorption band between ~480 nm and 660 nm is well established, but there is considerable disagreement between the absolute cross sections determined in the different studies, even when experimental errors and the effects of instrument resolution are accounted for. The values at 548.6 nm range from $(1.09 \pm 0.21) \times 10^{-17}$ to $(3.5 \pm 1.5) \times 10^{-17} \text{ cm}^2$. The preferred absorption cross section is the lower limit value from the study of Ingham *et al.*⁴ and represents a compromise between the high and low values reported. The uncertainty covers the range of reported values.

Vibrational assignments of the $\tilde{A}-\tilde{X}$ band system and positions of the vibronic band centers between 15120 cm^{-1} and 20753 cm^{-1} (482 nm to 661 nm) are tabulated in Himmelmann *et al.*¹

Dissociation of OIO into O(³P) + IO following absorption in the $\tilde{A}-\tilde{X}$ band system can be excluded on thermodynamic grounds. This is confirmed by the results of Ingham *et al.*⁴ who were unable to detect O atoms and report an upper limit of 0.007 for Φ_2 at 532 nm. Ingham *et al.*⁴ also report an upper limit of ~0.15 on the value of Φ_1 , but the results of Ashworth *et al.*⁵ provide compelling evidence that the ²B₂ upper state is strongly predissociated, and they report quantum calculations that efficient dissociation to I + O₂ can occur. This issue is unresolved and no recommendation is made for Φ_1 .

References

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- ³ R. A. Cox, W. J. Bloss, R. L. Jones, and D. M. Rowley, *Geophys. Res. Lett.* **26**, 1857 (1999).
- ⁴ T. Ingham, M. Cameron, and J. N. Crowley, *J. Phys. Chem. A* **104**, 8001 (2000).
- ⁵ S. H. Ashworth, B.J. Allen and J. M. C. Plane, *Geophys Res.Lett.*, **29**, 10.1029/2001GL013851, (2002).
- ⁶ Y. Bedjanian, G. LeBras, and G. Poulet, *J. Phys. Chem. A* **102**, 10501 (1998).