

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PI2

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HOI + hν → products

Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HOI + hν → HO + I	(1)	236	507
→ HI + O(³ P)	(2)	366	327
→ IO + H	(3)	415	288
→ HI + O(¹ D)	(4)	555	216

Absorption cross-section data

Wavelength range/nm	Reference	Comments
280-500	Bauer <i>et al</i> , 1998 ¹	(a)
278-494	Mossinger <i>et al</i> , 1999 ²	(b)

Comments

- (a) Laser photolysis of H₂O at 240 nm was used to produce HO radicals in the presence of I₂, and hence to produce HOI *in situ*. Absorptions were measured by a gated diode array, and at selected wavelengths by a photomultiplier. The HOI concentration was determined from the instantaneous I₂ loss. The spectrum consists of two unstructured bands at 340.4 nm [$\sigma_{\text{max}} = (3.85 \pm 0.4) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$] and 406.4 nm [$\sigma_{\text{max}} = (3.30 \pm 0.3) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$].
- (b) Same technique as in comment (a). Some irreproducibility in the 406 nm band was tentatively attributed to I₂O formation.

Quantum yield data

Quantum yield	Wavelength/nm	Reference	Comments
$\phi = 1.05 \pm 0.13$	355	Bauer <i>et al.</i> , 1999 ¹	(a)

- (a) HOI was produced by pulsed laser photolysis of HNO₃ at 248 nm to produce HO radicals in the presence of I₂. A second 355 nm laser pulse interrogated the HOI produced and the photofragment product HO was observed by resonance fluorescence. Fresh reactants were

introduced at each laser pulse. The quantity $\{\sigma^{\text{HOI}}\phi(\text{OH})^{\text{HOI}}\}$ at 355 nm was determined which, with the measured value of σ (see above), gave the cited value of ϕ .

Preferred Values

Absorption cross-sections of HOI at 295 K

λ/nm	$10^{19} \sigma/\text{cm}^2$	λ/nm	$10^{19} \sigma/\text{cm}^2$
280	0.0077	390	2.66
285	0.0226	395	2.98
290	0.0589	400	3.22
295	0.137	405	3.32
300	0.286	410	3.27
305	0.541	415	3.07
310	0.926	420	2.75
315	1.45	425	2.35
320	2.07	430	1.92
325	2.72	435	1.50
330	3.29	440	1.13
335	3.70	445	0.813
340	3.85	450	0.563
345	3.77	455	0.376
350	3.47	460	0.242
355	3.04	465	0.150
360	2.58	470	0.0904
365	2.21	475	0.0525
370	1.98	480	0.0296
375	1.94	485	0.0161
380	2.07	490	0.0086
385	2.33		

Quantum Yields

$\phi(1) = 1.0$ in the wavelength range 280-490 nm.

Comments on Preferred Values

The recommended values for the cross-sections are those given by Bauer *et al.*¹ The data of Mossinger *et al.*² are in good agreement with the exception of some systematically higher values in the 405 nm band. The original work of Jenkin,³ on which our previous evaluation, IUPAC, 1997⁴ was based, is qualitatively in agreement with the preferred values.

References

- ¹ D. Bauer, T. Ingham, S.A. Carl, G.K. Moortgat, and J.N. Crowley, *J. Phys. Chem. A.*, **102**, 2857 (1998).
- ² J.A. Mossinger, *J. Atmos. Chem.*, **34**, 137, (1999).
- ³ M.E. Jenkin, Ph.D. Thesis, University of East Anglia (1991).
- ⁴ IUPAC, Supplement V, 1997 (see references in Introduction).