

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PCI3

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OCIO + hv → products

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
OCIO + hv → ClO + O(³ P) (1)	255	470
→ Cl + O ₂ (2)	26	4540

Preferred Values

Absorption cross-sections of OCIO at the band peaks at 204 K, 296 K and 378 K

Band	λ/nm	$10^{20} \sigma/\text{cm}^2$		
		204 K	296 K	378 K
a(0)	475.53		13	
a(1)	461.15	17	17	16
a(2)	446.41	94	69	57
a(3)	432.81	220	166	134
a(4)	420.58	393	304	250
a(5)	408.83	578	479	378
a(6)	397.76	821	670	547
a(7)	387.37	1046	844	698
a(8)	377.44	1212	992	808
a(9)	368.30	1365	1136	920
a(10)	359.73	1454	1219	984
a(11)	351.30	1531	1275	989
a(12)	343.44	1507	1230	938
a(13)	336.08	1441	1139	864
a(14)	329.22	1243	974	746
a(15)	322.78	1009	791	628
a(16)	317.21	771	618	516
a(17)	311.53	542	435	390
a(18)	305.99	393	312	291
a(19)	300.87	256	219	216
a(20)	296.42	190	160	167
a(21)	291.77	138	114	130
a(22)	287.80	105	86	105
a(23)	283.51	89	72	90
a(24)	279.64	73	60	79
a(25)	275.74	59	46	
a(26)	272.93	53	33	

Quantum yields for OCIO photolysis at 298 K

$\phi_1 = 1.0$ over the wavelength range 270-480 nm.

$\phi_2 < 0.04$ between 365 and 450 nm.

Comments on Preferred Values

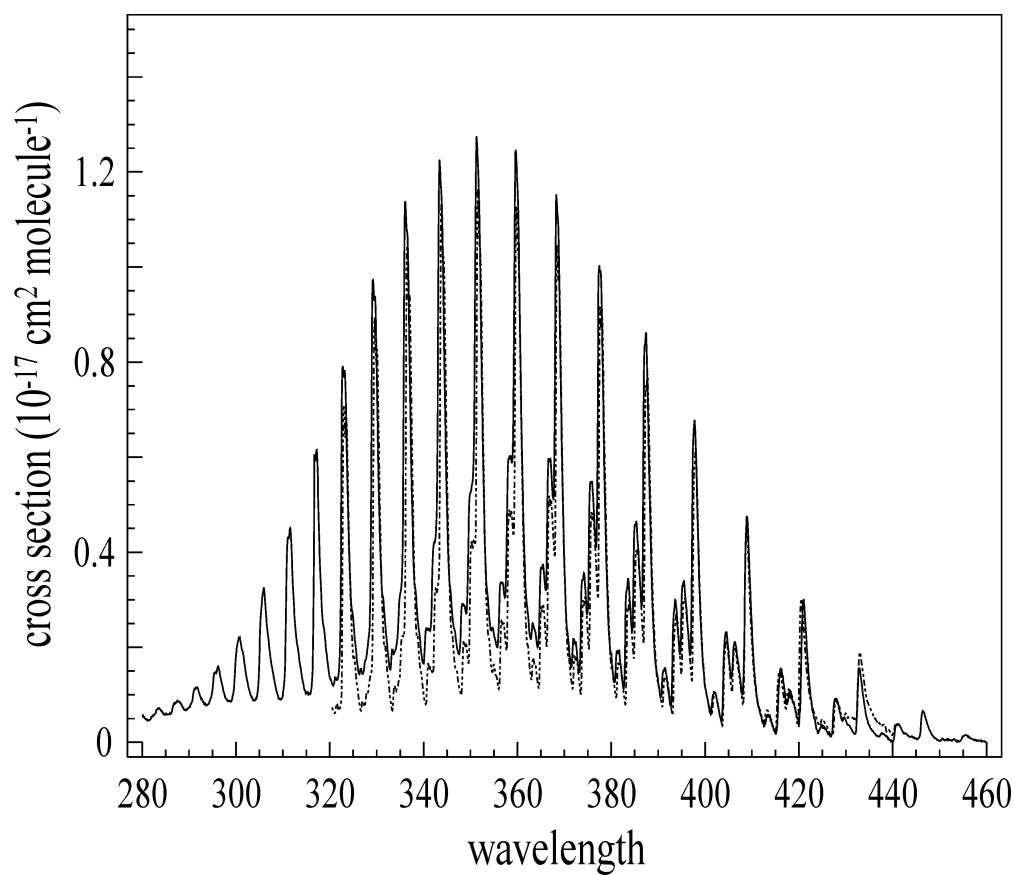
The preferred values of the absorption cross-sections at the peak of the bands [a(0) to a(26)] at 204 K, 296 K, and 378 K are the values reported by Wahner et al. (1987). The bands become appreciably sharper with decreasing temperature (Wahner et al., 1987). However, the integrated band intensities remain constant for all bands between 204 K and 296 K, and, therefore, the solar photolysis rate is not expected to have a significant temperature dependence. Spectra have been obtained over a different temperature range (213-293 K) at higher resolution and, using Fourier transform methods, with better wavelength accuracy by Kromminga et al. (2003). In wavelength regions where data overlap, there is generally good agreement in the cross section, though Kromminga et al. (2003) note some wavelength inconsistencies, presumably errors in the wavelength calibration by Wahner et al. (1987). For this reason, the Kromminga et al. data may be more suited for retrieval of OCIO concentrations from high resolution absorption measurements. Photoabsorption measurements of OCIO over the wavelength range of 125 to 470 nm at 298 K have been carried out by Hubinger and Nee (1994). Absorption cross-sections as a function of vibrational excitation are reported.

The recommended quantum yield of unity for O-atom production is based on results reported by Colussi (1990), and results of earlier studies discussed by Watson (1977). Vaida and co-workers (Vaida et al., 1989; Ruehl et al., 1990) reported the detection of Cl atoms by resonance-enhanced multiphoton ionisation (REMPI) in the photoisomerization of OCIO to ClOO followed by dissociation to Cl + O₂. Bishenden et al. (1991), using REMPI detection of Cl atoms, report that the quantum yield for Cl atom formation near 360 nm is 0.15 ± 0.10 . In contrast, Lawrence et al. (1990), using a technique involving charge transfer excitation of Cl-Xe collision pairs as a sensitive probe of Cl atoms, determined that the quantum yield for Cl atom production in the 359-368 nm region is $< 5 \times 10^{-4}$. In a molecular beam-photofragment study over the wavelength range 350-475 nm, Davis and Lee (1992) observed the dominant products to be ClO + O and also observed Cl atom yields reaching a maximum of 3.9% near 404 nm, decreasing to $< 0.2\%$ in the wavelength range 350-370 nm, in qualitative agreement with the results of Lawrence et al. (1990). More recent experiments of Davis and Lee (1996) show that the quantum yield for Cl + O₂ production is $3.9 \pm 0.8\%$ at 404 nm, decreasing at longer and shorter wavelengths, and the branching ratio between the channels (1) and (2) depends on the OCIO excited state vibrational mode. Delmdahl et al. (1998) observed nascent Cl atom formation between 360 and 450 nm. A quantum yield less than 3.6% was determined between 365 and 450 nm. Below 365 nm Cl atom formation resulting from the photolysis of vibrationally excited ClO ($v \geq 4$) radicals was observed.

References

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Absorption cross sections of OCIO: The solid line from Wahner et al. (1987) at 296 K and resolution of 0.07 nm. The dotted line of Kromminga et al. (2003) at 293 K and 20 cm⁻¹ resolution.