$CH_2OO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH /kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_2OO + h\upsilon \rightarrow CH_2O + O(^3P)$	(1)	185	645
$\rightarrow CH_2O + O(^1D)$	(2)	292	410

Absorption cross-section data

Wavelength range/nm	Reference	Comments
280 – 410	Beames et al., 2012	(a)
300 – 445	Sheps, 2013	(b)
280 – 500	Ting et al., 2014	(c)
375	Buras et al., 2014	(d)
362 – 470	Foreman et al., 2015	(e)

Comments

(a) CH_2OO prepared by PLP (248 nm) of CH_2I_2 in O_2/Ar mixtures in a capillary tube. The photoproducts were cooled in a supersonic expansion and passed to a TOF mass spectrometer where they were ionised with VUV radiation at 118 nm. The signal at *m/z* 46 detected when 248 nm photolysis occurred in the capillary, was attributed to CH_2OO. The UV absorption spectrum was determined from depletion of the *m/z* 46 photo-ionisation signal resulting from excitation of the B $\leftarrow$ X transition in ground state CH_2OO molecules by tunable UV radiation (280 – 420 nm) Nd-YAG laser. The absorption followed a simple Gaussian form with a peak at 335 nm and a breath (fwhm) of 40 nm. The cross section at the maximum of the absorption band at 335 nm was estimated to be approximately 5×10^{-17} cm^2 molecule^{-1}.

(b) CH_2OO prepared by PLP (266 nm) of CH_2I_2 in O_2/Ar mixtures at 5.1 Torr pressure. Absorption of CH_2OO in presence of excess SO_2 was observed by time-resolved UV absorption spectrum. Chemical kinetics measurements of its reactivity establish the identity of the absorbing species as CH_2OO. Separate measurements of the initial CH_2I radical concentration were used to determine the absolute absorption cross section of CH_2OO. The value obtained at the peak of the absorption band, 355 nm, was $\sigma = (3.6 \pm 0.9) \times 10^{-17}$ cm^2 molecule^{-1}. The difference between the absorption and action spectra was attributed to excitation to long-lived $\tilde{B}$ ($^1A'$) vibrational states that may relax to lower electronic states by fluorescence or nonradiative processes. Spectral resolution was ~1 nm.

(c) CH_2OO was prepared by pulsed 248 nm photolysis of CH_2I_2/O_2 mixtures; transient absorption spectra were recorded using a gated intensified CCD camera (1 ms gate width). Spectral resolution was 2 nm. Decay of CH_2OO by self-reaction and by

reaction with SO_2 were utilized to extract the absorption spectrum of CH_2OO, corrected for contributions by other absorbers. The peak cross section is $(1.26 \pm 0.25) \times 10^{-17}$ cm^2 molecule^{-1} at 340 nm, based on the quantum efficiency of CH_2OO production ($\phi_{CH2OO} = 0.86$ at 11 Torr, reported by Stone et al. 2013). Absolute absorption cross-sections of CH_2OO were also obtained from laser-depletion measurements in a jet-cooled molecular beam with the laser fluence calibrated using a reference molecule. Values from the laser-depletion measurements, $\sigma = (8.09 \pm 0.90) \times 10^{-18}$ at 308.4 nm and $(1.21 \pm 0.13) \times 10^{-17}$ cm^2 molecule^{-1} at 351.8 nm, are consistent with results from absorption measurements taking into account uncertainties in spectral overlap at different resolution and gas temperature.

(d) CH_2OO was produced by the $CH_2I + O_2 \rightarrow CH_2OO + I$ reaction following 355 nm laser photolysis of CH_2I_2 in a large excess of O_2. CH_2OO kinetics were followed by time resolved absorption at 375 nm in the $B \leftarrow X$ transition and the atomic I co-product followed by probing the 1315.246 nm $F = 3$ $^2P_{1/2} \leftarrow F = 4$ $^2P_{3/2}$ atomic transition. $[CH_2OO]_0$ was determined by simultaneous fitting of the decay of $[I]$ and $[CH_2OO]$. The absorption cross section of CH_2OO at the UV probe wavelength ($\lambda = 375$ nm) was derived as $(6.2 \pm 2.2) \times 10^{-18}$ cm^2 molecule^{-1}.

(e) CH_2OO was produced by the $CH_2I + O_2 \rightarrow CH_2OO + I$ reaction following the 355 nm laser photolysis of CH_2I_2/O_2 mixtures in 50-70 Torr total pressure of N_2. Absorption spectra of CH_2OO were recorded using two different experimental techniques. First, conventional single-pass absorption spectroscopy using pulsed LED broadband light sources to measure the spectra over the range 362-470 nm. Second, pulsed cavity ring down spectroscopy to record high resolution spectra over the range 417-435 nm. In both systems $[CH_2OO]_0$ was calculated from the CH_2I_2 concentration, CH_2I_2 absorption cross section, laser fluence, and CH_2OO yield in the $CH_2I + O_2$ reaction. Over the wavelength range where the two techniques overlapped there was good agreement in the spectra obtained using the different experimental approaches. The absorption cross section at 375 nm is 6×10^{-18} cm^2 molecule^{-1}.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\,\sigma/(cm^2$ molecule$^{-1})$	λ/nm	$10^{20}\,\sigma/(cm^2$ molecule$^{-1})$	λ/nm	$10^{20}\,\sigma/(cm^2$ molecule$^{-1})$
280	190	340	1230	400	345
285	290	345	1215	405	190
290	380	350	1200	410	230
295	490	355	1125	415	110
300	551	360	1050	420	120
305	660	365	1004	425	45
310	785	370	844	430	50
315	920	375	767	435	30
320	979	380	720	440	0
325	1075	385	455	445	0
330	1140	390	520	450	0
335	1195	395	300	455	0

$\sigma = (1.23 \pm 0.18) \times 10^{-17}$ cm^2 molecule^{-1} at λ_{max} (340 nm)

Quantum Yields

$\phi_1 = 1.0$ for $280 < \lambda < 420$ nm.

Comments on Preferred Values

All reported studies of UV absorption by the formaldehyde oxide Criegee intermediate show a strong absorption band in the mid UV region attributed to the $\tilde{B}$ (1A′) ← $\tilde{X}$(1A′) electronic transition. However, the results are not all in good agreement, either in absolute magnitude of the cross section at the absorption maximum, or in the overall shape of the spectrum (e.g., see Figure 1 in Foreman et al. 2015 and Figure 4 in Ting et al. 2014). The UV photo-dissociation action spectrum reported by Beames et al. (2012) differs substantially from the absorption spectrum reported by Sheps (2013) with the latter extending to longer wavelengths and exhibiting resolved vibrational structure on its low-energy side. The cross-section estimate of Beames et al. (2012) was based on a laser fluence estimated without correction for beam non-uniformity. Ting et al. (2014) used both multiplex long-path UV absorption and the photo-dissociation action technique, to give improved accuracy to determine cross-sections over a wide range of wavelengths. The shape of the spectra reported by Ting et al. (2014) and Sheps (2013) agree well for $\lambda > 345$ nm but there is clear and unexplained conflict at $\lambda < 345$ nm, where the absorption falls off much more rapidly in the spectrum reported by Sheps (2013). Explanations of the differences in shape based on strong temperature dependence at longer wavelengths (analogy to the Hartley/Huggins bands in iso-electronic O_3 molecule), and a proposed decrease in the dissociation yield at long wavelengths (Sheps, 2013) due to competing processes are not consistent with the body of photophysical information. The single wavelength determination of σ (375) nm of Buras et al. (2014), as part of their kinetic study of the CH_2OO self-reaction, is in good agreement with the results of Ting et al. (2014). Foreman et al. (2015) used both conventional UV absorption spectroscopy and cavity ring down spectroscopy to study the CH_2OO spectrum at 362-470 nm and reported results which are in excellent qualitative and quantitative agreement with those from Ting et al. (2014) and Buras et al. (2013).

There is excellent agreement in the results reported by Buras et al. (2013), Ting et al. (2014), and Foreman et al. (2015). The preferred value of the cross section at the λ_{max} in the B-X transition is based on those measured by Ting et al. (2014), in their jet cooled measurements, i.e. values obtained at 308.4 and 351.8 nm were: $(8.09 \pm 0.90) \times 10^{-18}$ and $(1.21 \pm 0.13) \times 10^{-17}$ cm^2 molecule^{-1} respectively. These values are expected to have very weak temperature dependence by analogy with O_3 Hartley band (and Foreman et al. (2015) have demonstrated that the cross-sections between 362 nm and 470 nm are independent of temperature over the range 276-357 K). The cross-sections at discrete wavelengths over the range 280-500 nm were obtained by Ting et al. (2014), by scaling their absorption data to the above data points near λ_{max}. The IUPAC recommended peak cross section at 340 nm and cross-sections at 5 nm intervals are evaluated by averaging data from their analysis. The error of ±15% includes possible variations arising from the temperature effects. The photodissociation quantum yields of CH_2OO are likely to be close to unity since the product anisotropy measured by Lehman et al. (2013) shows that dissociation occurs faster than rotation of the CH_2OO molecule.

References

Beames, J. M., Liu, Fang Lu, Lu Lu, and Lester, M. I.: J. Amer. Chem. Soc., 134, 20045, 2012.
Buras, Z. J., Elsamra, R. M. I., and Green, W. H: J. Phys. Chem. Lett., 5, 2224, 2014.

Foreman, E. S., Kapnas, K. M., Jou, Y., Kalinowski, J., Feng, D., Gerber, R. B., and Murray, C.: Phys. Chem. Chem. Phys., 17, 32539, 2015.
Lehman, J. H., Li, H., Beames, J. M., and Lester, M. I.: J. Chem. Phys., 139, 141103, 2013.
Sheps, L.: J. Phys. Chem. Lett., 4, 4201, 2013.
Ting,W-L, Chen, Y-H., Chao, W., Smith, M.C., and Lin, J Jr -M.: Phys. Chem. Chem. Phys., 16, 10438, 2014.
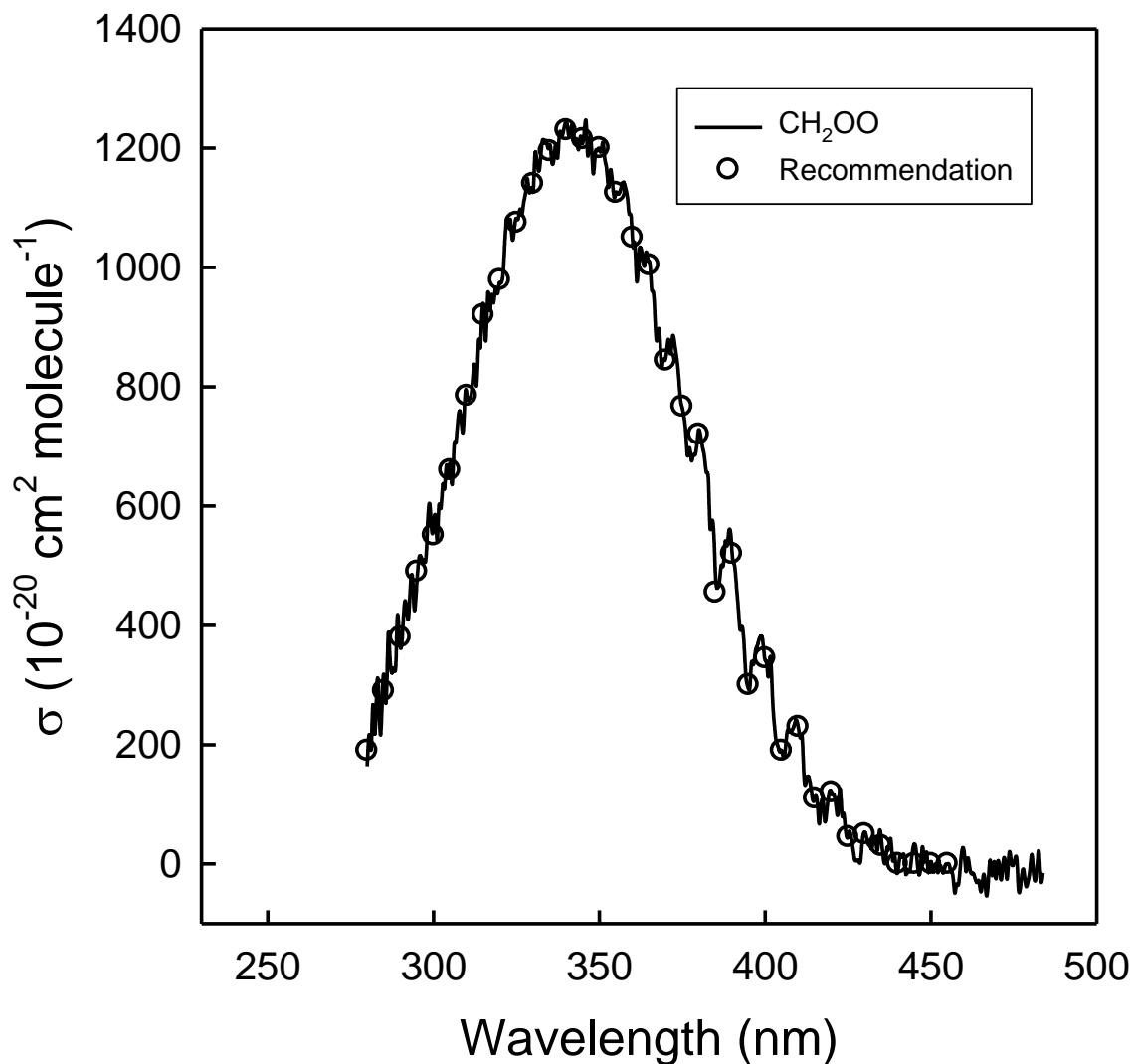
UV absorption cross sections of CH₂OO (using the SO₂ scavenging method) reported by Ting et al. (2014) and recommended values.