

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, Data Sheet P34

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CH₃CHOO (*Z*- and *E*-) + hν → products

Primary photochemical transitions

Reaction	
CH ₃ CHOO + hν → CH ₃ CHO + O(³ P)	(1)
→ CH ₃ CHO + O(¹ D)	(2)

Absorption cross-section data

Wavelength range/nm	Reference	Comments
280 – 410	Beames et al., 2013	(a)
300 – 445	Sheps et al., 2014	(b)
280 – 500	Smith et al., 2014	(c)

Comments

- (a) CH₃CHOO prepared by PLP (248 nm) of CH₃CHI₂ in O₂/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 CH₃CHOO. Both *Z*- and *E*- conformers of the acetaldehyde oxide species were formed in the process. The UV absorption spectrum was determined from depletion of the *m/z* 46 photo-ionisation signal resulting from excitation of the B ← X transition in ground state CH₃CHOO molecules by tunable UV radiation (280 – 420 nm) from a Nd-YAG laser. The UV-induced depletion approaches 100% near the peak of the simple Gaussian profile at 320 nm, indicating rapid dynamics in the *B* state, and corresponds to a peak absorption cross section of $\sim 5 \times 10^{-17}$ cm² molecule⁻¹; the absolute cross section measurements have an uncertainty on the order of a factor of 2.
- (b) CH₃CHOO prepared by PLP (266 nm) of CH₃CHI₂ in O₂/Ar mixtures at 5.1 Torr pressure. Absorption of CH₃CHOO in the absence and presence of excess SO₂ or H₂O was observed by time-resolved UV absorption spectrum at 300 – 425 nm. Spectral resolution was ~ 1 nm. Absorption features due to the B ← X transition in ground state of *Z*- and *E*- conformers of CH₃CHOO could be distinguished by their differing reactivities - reflected in characteristic time dependencies for decay of these absorption features. The absorption band for *Z*-CH₃CHOO peaked at 323 nm, with a 40 nm FWHM. For *E*-CH₃CHOO, FWHM was 35 nm centred at 360 nm. Estimates of the absolute absorption cross sections of the two conformers was based on the value obtained by Smith et al (2014), using the ion depletion method, for *Z*-CH₃CHOO at 308 nm, where only the *Z*- conformer absorbs. The value obtained at the peak of the *Z*-CH₃CHOO absorption band at 323 nm was $\sigma = 1.2 \times 10^{-17}$ cm² molecule⁻¹, and at

the peak of the *E*-CH₃CHOO absorption at 360 nm was $\sigma = 1.2 \times 10^{-17}$ cm² molecule⁻¹.

- (c) CH₃CHOO was prepared by pulsed-248 nm photolysis of CH₃CHI₂/O₂ mixtures. Transient absorption spectra (260 – 500 nm; resolution 1.5 nm) were recorded using a gated iCCD spectrometer. Decays of CH₃CHOO by self-reaction and by reaction with SO₂ were utilized to extract the absorption spectrum of CH₂OO, corrected for contributions by other absorbers. Absolute absorption cross-sections of CH₃CHOO were obtained from laser-depletion measurements in a jet-cooled molecular beam (as described by Ting et al 2014 for CH₂OO), using EI-MS to monitor C₂H₄OO⁺ at *m/z* = 60. The laser fluence at 308 and 352 nm was calibrated directly (from laser beam profiling measurements) and by using the observed laser depletion of CH₃CHI₂ and the literature absorption cross section for CH₃CHI₂ at 308 nm. From the relative laser fluence for the CH₃CHOO and CH₃CHI₂ experiments the cross-section ratio $\sigma(\text{CH}_3\text{CHOO})/\sigma(\text{CH}_3\text{CHI}_2)$, and hence $\sigma(\text{CH}_3\text{CHOO})$ at 308 nm was calculated. Consistent results for $\sigma(\text{CH}_3\text{CHOO})$ at 308 nm were obtained using the two different calibration methods. The values obtained at 308 and 352 nm were: $(1.06 \pm 0.09) \times 10^{-17}$ and $(9.7 \pm 0.0.6) \times 10^{-17}$ cm² molecule⁻¹, respectively. These values were consistent with the relative broad band absorption measurements at these wavelengths and were used to calibrate the spectrum to provide absolute cross sections over the range 280 – 480 nm. The peak cross section is $\lambda_{\text{max}} = (1.27 \pm 0.11) \times 10^{-17}$ cm² molecule⁻¹ at 328 nm.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20} \sigma/(\text{cm}^2 \text{ molecule}^{-1})$	λ/nm	$10^{20} \sigma/(\text{cm}^2 \text{ molecule}^{-1})$	λ/nm	$10^{20} \sigma/ \text{cm}^2 \text{ molecule}^{-1})$
280	428	340	1176	400	117
285	528	345	1101	405	83
290	638	350	1008	410	58
295	752	355	902	415	39
300	867	360	788	420	26
305	976	365	673	425	17
310	1074	370	562	430	11
315	1155	375	458	435	7
320	1214	380	365	440	4
325	1247	385	284	445	2
330	1251	390	217	450	1
335	1227	395	161	455	0

Gaussian fit parameters to data of Smith et al. (2014): $\sigma(\lambda) = 1253.16 \times \exp(-0.000460967 \times (328.28 - \lambda)^2)$

Absorption cross-sections at 298 K (conformer resolved)

λ/nm	$10^{20} \sigma (Z-)/(\text{cm}^2 \text{ molecule}^{-1})$	$10^{20} \sigma (E-)/(\text{cm}^2 \text{ molecule}^{-1})$
300	847	209
310	1180	287
330	1150	913
350	906	1070
370	318	1200
390	59	965
410	12	652

$$\sigma(Z-) = (1.20 \pm 0.18) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1} \text{ at } \lambda_{\text{max}} (323 \text{ nm})$$

$$\sigma(E-) = (1.20 \pm 0.18) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1} \text{ at } \lambda_{\text{max}} (360 \text{ nm})$$

Gaussian fit parameters to data for *Z*-CH₃CHOO: $\sigma(\lambda) = 1253.18 \times 10^{-20} \exp(-0.00060787 \times (324.11 - \lambda)^2)$.

Gaussian fit parameters to data for *E*-CH₃CHOO: $\sigma(\lambda) = 1228.72 \times 10^{-20} \exp(-0.00037271 \times (365.53 - \lambda)^2)$

Quantum Yields

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

Comments on Preferred Values

All reported studies of UV absorption by the acetaldehyde oxide Criegee intermediate show a broad Gaussian band peaking at about 320 nm with weak structure on the long-wavelength side, which is attributed to the $\tilde{B}(1A') \leftarrow \tilde{X}(1A')$ electronic transition. The results from techniques using absorption spectroscopy (Sheps et al., 2013; Smith et al., 2014), and using the UV photo-dissociation action spectrum of CH₃CHOO of Smith et al. (2014), are in good agreement on the overall shape of the spectrum. However, the action spectrum reported by Beames et al. (2013) differs substantially from the other studies in that the band is narrower (FWHM = 37 nm vs 77 nm), and the peak cross section determined from photo-dissociation action spectrum at $\lambda = 320$ nm is a factor of 4 higher than by Smith et al. (2014). Smith et al. (2014) also used the photo-dissociation action technique with direct laser fluence measurements to give improved accuracy for $\sigma(\text{CH}_3\text{CHOO})$ at 352 nm and 308 nm. They also measured the cross-section ratio $\sigma(\text{CH}_3\text{CHOO})/\sigma(\text{CH}_3\text{CHI}_2)$ at 308 nm, and determined $\sigma(\text{CH}_3\text{CHOO})$ based on the known value for $\sigma(\text{CH}_3\text{CHI}_2)$ at this wavelength. These results agreed and were combined with multiplex long-path UV absorption to determine $\sigma(\text{CH}_3\text{CHOO})$ over a wide range of wavelengths. These form the basis of the preferred cross sections in this evaluation. 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 first figure below shows the values reported by Smith et al. and a Gaussian fit to these data. The error of $\pm 15\%$ includes possible variations arising from the temperature effects.

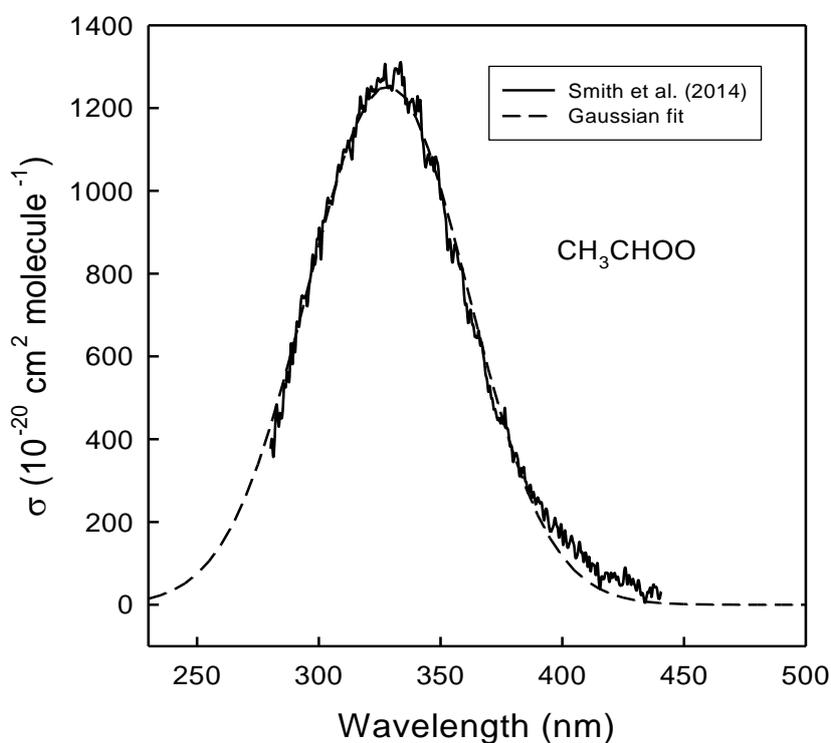
The source chemistry produces CH₃CHOO in two (stable) conformers: *Z*- and *E*-, which differ in the orientation of the O-O moiety relative to the CH₃- group. Only the study of Sheps et al. (2014) provides cross sections for the individual conformers, by extracting their spectral contributions to the overall absorption band, using their different decay times (175 ± 25 and $2800 \pm 300 \text{ s}^{-1}$ for *Z*- and *E*- CH₃CHOO, respectively) in the presence of $1 \times 10^{17} \text{ cm}^{-3} [\text{H}_2\text{O}]$. The sum of absorption components for *Z*- and *E*-CH₃CHOO extrapolated to $t = 0$, agree well with the overall spectra reported by Smith et al. (2014), and are consistent with initial production of $\sim 30\%$ of total CH₃CHOO in the *E*-conformer. The IUPAC preferred cross sections at 5 nm intervals were calculated by fitting a Gaussian to the retrieved conformer-resolved cross-sections (see the second figure below). The error of $\pm 30\%$ on the conformer cross-sections arises mainly from the fitting procedure used to deconvolute the overlap of the conformer spectra. The UV spectrum of *Z*-CH₃CHOO is centered at 323 nm and has FWHM of ~ 40 nm, whilst the peak cross section of the *E*-conformer is ~ 360 nm. Both conformers have approximately equal cross-sections at the peak. The spectral features are consistent with theoretical calculations where a combination of ground state stabilization and excited state destabilization shifts the vertical *B*-*X* transition for *Z*-CH₃CHOO (< 3.8 eV) to higher energy, and correspondingly shorter wavelength, than those for *E*-CH₃CHOO (< 3.5 eV) and CH₂OO (< 3.6 eV), in each case starting from the equilibrium configuration.

The photodissociation quantum yields are likely to be close to unity (Lehman et al., 2013). Hydroxyl radicals produced concurrently with the generation of the Criegee intermediates (from the reactions of CH₃CHI and CH₂I with O₂) were measured in the

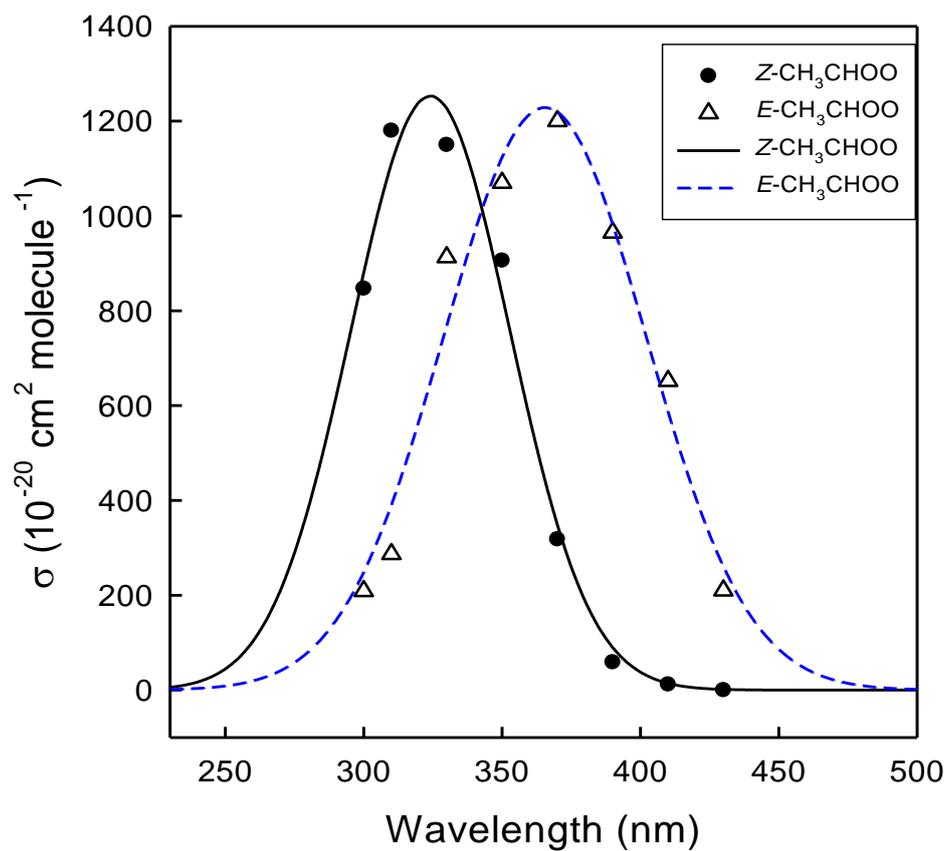
experiments of Beames et al. (2013), where they were detected by 1+1' resonance enhanced multiphoton ionization. The OH yield observed with CH₃CHOO is 4-fold larger than that from CH₂OO, consistent with prior studies of OH generation from alkene ozonolysis.

References

- Beames, J. M., Liu, F., Lu L., and Lester, M. I.: J. Chem. Phys. 138, 244307, 2013.
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Smith, M.C., Ting, W-L., Chang, C-H., Takahashi, K., Boering, K.A., and Lin, J. Jr -M.: J. Chem. Phys., 141, 074302, 2014.



Absorption spectrum of CH₃CHOO, *Z*- and *E*- conformers not resolved; Gaussian fit to experimental data (from Smith et al., 2014) shown as dashed line.



Absorption spectrum of CH₃CHOO, Z- and E- conformers resolved (shown as circles and triangles, respectively); Gaussian fits to experimental data (from Sheps et al., 2014) shown as dotted lines.