

### IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P34

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#### Primary photochemical transitions

Reaction		$\Delta H_{298}^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{CHOO} + h\nu \rightarrow \text{CH}_3\text{CHO} + \text{O}({}^3\text{P})$	(1)	185	645
$\rightarrow \text{CH}_3\text{CHO} + \text{O}({}^1\text{D})$	(2)	292	410

#### 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)  $\text{CH}_3\text{CHOO}$  prepared by PLP (248 nm) of  $\text{CH}_3\text{CHI}_2$  in  $\text{O}_2/\text{Ar}$  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 118nm. The signal at  $m/z$  46 detected when 248nm photolysis occurred in the capillary, was attributed to  $\text{CH}_3\text{CHOO}$ . Both *syn- and anti-* 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  $B \leftarrow X$  transition in ground state  $\text{CH}_3\text{CHOO}$  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  $\sim 5 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ ; the absolute cross section measurements have an uncertainty on the order of a factor of 2. The electronic spectrum for  $\text{CH}_3\text{CHOO}$  is similar to that reported recently for  $\text{CH}_2\text{OO}$ , but shifted 15 nm to shorter wavelength.
- (b)  $\text{CH}_3\text{CHOO}$  prepared by PLP (266 nm) of  $\text{CH}_3\text{CHI}_2$  in  $\text{O}_2/\text{Ar}$  mixtures at 5.1 Torr pressure. Absorption of  $\text{CH}_3\text{CHOO}$  in the absence and presence of excess  $\text{SO}_2$  or  $\text{H}_2\text{O}$  was observed by time-resolved UV absorption spectrum at 300 – 425 nm. Spectral resolution was  $\sim 1$  nm.

Absorption features due to the  $B \leftarrow X$  transition in ground state of *syn* and *anti* conformers of  $\text{CH}_3\text{CHOO}$  could be distinguished by their differing reactivities - reflected in characteristic time dependencies for decay of these absorption features. The absorption band for the *syn*- $\text{CH}_3\text{CHOO}$  absorption band peaked at 323 nm, with a 40nm FWHM, and for the *anti*- $\text{CH}_3\text{CHOO}$ , FWHM was 35nm FWHM 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 *syn*- $\text{CH}_3\text{CHOO}$  at 308 nm, where only the *syn* conformer absorbs. The values obtained at the observed peaks of the *syn*- $\text{CH}_3\text{CHOO}$  absorption band, 323 nm, was  $\sigma = 1.2 \times 10^{-17} \text{ cm}^2$ , and for the peak *anti*- $\text{CH}_3\text{CHOO}$  absorption at 360 nm, was  $\sigma = 1.2 \times 10^{-17} \text{ cm}^2$ .

- (c)  $\text{CH}_3\text{CHOO}$  was prepared by pulsed-248 nm photolysis of  $\text{CH}_3\text{CHI}_2/\text{O}_2$  mixtures. Transient absorption spectra were recorded using a gated iCCD spectrometer (1 ms gate width), after the probe light was dispersed using a grating monochromator. Spectral resolution was 1.5nm, and up to 18 spectra were recorded at delay times up to 484 ms over the spectral range 260 – 500 nm. Decay of  $\text{CH}_3\text{CHOO}$  by self-reaction and by reaction with  $\text{SO}_2$  were utilized to extract the absorption spectrum of  $\text{CH}_2\text{OO}$ , corrected for contributions by other absorbers, under reaction conditions. Absolute absorption cross-sections of  $\text{CH}_3\text{CHOO}$  were obtained from laser-depletion measurements in a jet-cooled molecular beam (as described by Ting et al 2014 for  $\text{CH}_2\text{OO}$ ), using EI-MS to monitor  $\text{C}_2\text{H}_4\text{OO}^+$  at  $m/z = 60$ . The laser fluence was calibrated with a reference molecule. The values obtained at 308 and 352 nm were:  $(1.06 \pm 0.09) \times 10^{-17} \text{ cm}^2$  and  $(9.7 \pm 0.6) \times 10^{-17} \text{ cm}^2$  respectively. These values were consistent with the 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  $\lambda_{\text{max}} = (1.27 \pm 0.11) \times 10^{-17} \text{ cm}^2$  at 328 nm. The peak wavelength is blue shifted by 14 nm from the  $\lambda_{\text{max}}$  for  $\text{CH}_2\text{OO}$  at 342 nm.

**Preferred Values**

**Absorption cross-sections at 298 K**

$\lambda/\text{nm}$	$\sigma/\text{cm}^{-2}$ $\times 10^{-20}$	$\lambda/\text{nm}$	$\sigma/\text{cm}^{-2}$ $\times 10^{-20}$	$\lambda/\text{nm}$	$\sigma/\text{cm}^{-2}$ $\times 10^{-20}$
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

$\sigma = (1.23 \pm 0.18) \times 10^{-17} \text{ cm}^2$  at  $\lambda_{\text{max}}$  (340 nm) ;

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

Mis en forme : Police :Symbol

**Absorption cross-sections at 298 K (conformer resolved)**

$\lambda/\text{nm}$	$\sigma(\text{syn})/\text{cm}^{-2}$ $\times 10^{-20}$	$\sigma(\text{anti})/\text{cm}^{-2}$ $\times 10^{-20}$
300	847	209
310	1180	287
330	1150	913
350	906	1070
370	318	1200
390	59	965
410	12	652
430	0	210

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

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

Gaussian fit parameters to data for *syn*-CH<sub>3</sub>CHOO:  $\sigma(\lambda) = 1253.18 \times 10^{-20} \exp(-0.00060787 \times (324.11 - \lambda)^2)$ .

Gaussian fit parameters to data for *anti*-CH<sub>3</sub>CHOO:  $\sigma(\lambda) = 1228.72 \times 10^{-20} \exp(-0.00037271 \times (365.53 - \lambda)^2)$

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### 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 Creigee diradical show a broad gaussian band peaking at about 320 nm with weak structure on the long-wavelength side, which is attributed to the in the  $\tilde{B}(1A') \leftarrow \tilde{X}(1A')$  electronic transition. Generally the results from techniques using absorption spectroscopy (Sheps et al., 2013; Smith et al., 2014), and using the UV photo-dissociation action spectrum of CH<sub>3</sub>CHOO 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 352nm and 308nm. They also measured the cross-section ratio  $\sigma(\text{CH}_3\text{CHOO})/\sigma(\text{CH}_3\text{CHI}_2)$  at 308nm, and determined  $\sigma(\text{CH}_3\text{CHOO})$  based 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 5nm intervals are evaluated by averaging data from their analysis. Fig 1 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 CH<sub>3</sub>CHOO in two (stable) conformers: *syn*- and *anti*- , which differ in the orientation of the O-O moiety relative to the CH<sub>3</sub>- group. Only the study of Sheps et al. (2104) provides cross sections for the individual conformers, by extracting their spectral contributions to the overall absorption band, using their different decay times ( $175 \pm 25$  and  $2800 \pm 300 \text{ s}^{-1}$ , for *syn*- and *anti*- CH<sub>3</sub>CHOO respectively ) in the presence of  $1 \times 10^{17} \text{ cm}^{-3} [\text{H}_2\text{O}]$ . The sum of absorption components for *syn*- and *anti*- CH<sub>3</sub>CHOO extrapolated to  $t = 0$ , agree well with the overall spectra reported by Smith et al. (2104), and are consistent with initial production of  $\sim 30\%$  of total CH<sub>3</sub>CHOO in the *anti*-conformer. The IUPAC preferred cross sections at 5 nm intervals were calculated by averaging data from their experiments. Fig 2 shows a Gaussian fit to the retrieved conformer-resolved cross-sections. 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 *syn*- CH<sub>3</sub>CHOO is centred at 323nm and has FWHM of  $\sim 40$  nm, whilst the peak cross section of the *anti*-conformer is  $\sim 360$  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 *syn*-CH<sub>3</sub>CHOO (<3.8 eV) to higher energy, and correspondingly shorter wavelength, than those for *anti*-CH<sub>3</sub>CHOO (<3.5 eV) and CH<sub>2</sub>OO (<3.6 eV), in each case starting from the equilibrium configuration.

The photodissociation quantum yields are likely to be close to unity. Hydroxyl radicals produced concurrently with the generation of the Criegee intermediates 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 CH<sub>3</sub>CHOO is 4-fold larger than that from CH<sub>2</sub>OO, consistent with prior studies of OH generation from alkene ozonolysis.

### References

- Beames, J. M., Liu, Fang Lu, Lu Lu, and Lester, M. I.: J. Chem. Phys. 138, 244307, 2013.  
Sheps, L., Scully, A.M. and Au, K., Phys.Chem.Chem.Phys. 16, 26701, 2014.  
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.  
Lehman, J.H., Li, H., Beames, J. M., and Lester, M. I.: J. Chem. Phys., 139, 141103, 2013

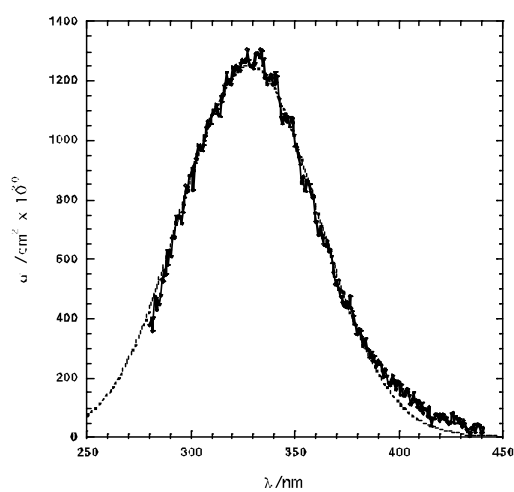


Figure 1: Absorption spectrum of CH<sub>3</sub>CHOO, *syn*- and *anti*- conformers not resolved; Gaussian fit to experimental data (from Smith et al., 2014) shown as dotted line.

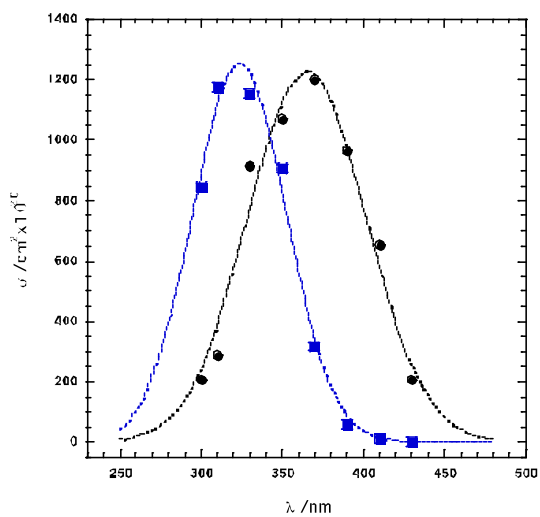


Figure 2 Absorption spectrum of  $\text{CH}_3\text{CHO}$ , *syn*- and *anti*- conformers resolved (shown as blue and black points, respectively); Gaussian fits to experimental data (from Sheps et al., 2014) shown as dotted line.