

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P35

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$(\text{CH}_3)_2\text{COO} + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$(\text{CH}_3)_2\text{COO} + h\nu \rightarrow (\text{CH}_3)_2\text{CO} + \text{O}(^3\text{P})$ (1)	185	645
$\rightarrow (\text{CH}_3)_2\text{CO} + \text{O}(^1\text{D})$ (2)	292	410

Absorption cross-section data

Wavelength range/nm	Reference	Comments
280-410	Liu et al., 2014	(a)

Comments

- (a) Acetone oxide, $(\text{CH}_3)_2\text{COO}$, was prepared by PLP (248 nm) of $(\text{CH}_3)_2\text{Cl}_2$ 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 118nm. The UV absorption spectrum was determined from depletion of the $m/z = 74$ photoionisation signal resulting from excitation of the $B \leftarrow X$ transition in ground state $(\text{CH}_3)_2\text{COO}$ 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 $\sim 4 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$; the absolute cross section measurements have an uncertainty on the order of a factor of 2. The electronic spectrum for $(\text{CH}_3)_2\text{COO}$ is similar to that reported from the same laboratory for CH_3CHOO .

Preferred Values

Absorption cross-sections at 298 K

λ/nm	σ/cm^{-2} $\times 10^{-20}$	λ/nm	σ/cm^{-2} $\times 10^{-20}$
280	175.7	345	2094
285	340.3	350	1464
290	609.1	355	946.5
295	1008	360	565.8
300	1543	365	312.8
305	2184	370	159.9
310	2858	375	75.55
315	3458	380	33.01
320	3869	385	13.34
325	4002	390	4.98
330	3828	395	1.72
335	3386	400	0.55
340	2769	405	0.16

$$\sigma = (4 \pm 2) \times 10^{-17} \text{ cm}^2 \text{ at } \lambda_{\text{max}} (324 \text{ nm}) ;$$

Gaussian fit parameters to data of Liu et al. (2014): $\sigma(\lambda) = 4 \times 10^{-17} \exp(-0.0015669 \times (324.6 - \lambda)^2)$

Quantum Yields

$$\phi_1 = 1.0 \text{ for } 280 < \lambda < 380 \text{ nm.}$$

Comments on Preferred Values

The only reported study of UV absorption spectrum of the acetone oxide Creigee diradical was obtained by Liu et al (2014), using UV photo-dissociation action technique. The source chemistry produces $(\text{CH}_3)_2\text{COO}$, which only has one stable conformer. The results show a Gaussian band peaking at 324 nm with no resolved structure, which is attributed to the in the $\tilde{\text{B}}(1\text{A}') \leftarrow \tilde{\text{X}}(1\text{A}')$ electronic transition in $(\text{CH}_3)_2\text{COO}$. No results have been reported to date for the $(\text{CH}_3)_2\text{COO}$ molecule using conventional absorption spectroscopy. However the results from the UV action spectra of several Criegee intermediates reported by the University of Pennsylvania group (e.g. CH_2COO and CH_3CHOO , Beames et al, (2012) and 2013) differs substantially from spectra recorded subsequently using conventional absorption spectroscopy (e.g. Sheps ,2013; Ting et al, 2014; Smith et al., 2014); in that the absorption band determined

from photo-dissociation action spectrum is narrower, peaks at a shorter wavelength, and the peak cross section is up to a factor of 4 higher than techniques using absorption spectroscopy (Sheps et al., 2013; Smith et al., 2014). Causes for this discrepancy remain unclear, as discussed in Ting et al., 2014 and Smith et al, 2014. The latter study 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. Results from the two methods were consistent for the three methods. The weight of evidence therefore favours the spectral shape and cross-sections determined by UV absorption and these form the basis of the preferred cross sections for CH_3CHOO in the IUPAC evaluation. In view of the implied uncertainty in the spectral parameters obtained by the UV photo-dissociation action technique we make no recommendation for the absorption cross sections for $(\text{CH}_3)_2\text{COO}$ at this time. Fig.1 shows the experimental values extracted from Fig.3 of the paper by Liu et al., (2014) and a Gaussian fit to these data. The listed cross-sections in the table are obtained from the Gaussian fit to the experimental data. The best estimate for absolute values for cross-sections near the peak are about a factor 3 lower than these listed values , but the uncertainty is large over the whole range.

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 Liu et al, (2013), where they were detected by 1+1' resonance enhanced multiphoton ionization. The OH yield observed with CH_3CHOO is 6-fold larger than that from CH_2OO , consistent with prior studies of OH generation from alkene ozonolysis (Kroll et al, 2002).

References

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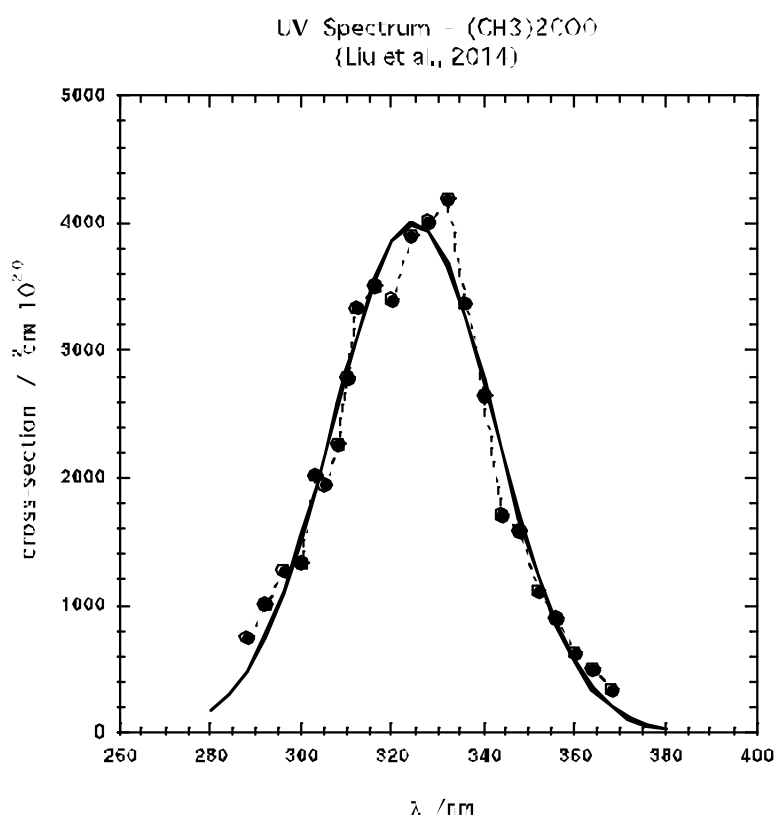


Figure 1: Absorption spectrum of $(\text{CH}_3)_2\text{CHOO}$; Gaussian fit to experimental data (from Liu et al., 2014) shown as full line.