IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P36

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CH_3CH_2CHOO + hν → products

Primary photochemical transitions

Reaction	
$CH_3CH_2COO + h\upsilon \rightarrow CH_3CH_2CO + O(^3P)$	(1)
$\rightarrow CH_3CH_2CO + O(^1D)$	(2)

Absorption cross-section data

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

Comments

(a) CH_3CH_2CHOO was prepared by PLP (248 nm) of $CH_3CH_2CHI_2$ 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 UV absorption spectrum was determined from depletion of the *m/z* =74 photo-ionisation signal resulting from excitation of the B ← X transition in ground state CH_3CH_2CHOO 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 325 nm, indicating rapid dynamics in the *B* state, and corresponds to a peak absorption cross section of ~3.5×10^{-17} cm^2 $molecule^{-1}$. The absolute cross section measurements have an uncertainty on the order of a factor of 2. The electronic spectrum for CH_3CH_2CHOO is similar to that reported for CH_3CHOO.

Preferred Values

Absorption cross-sections at 298 K relative to value at 320 nm

λ/nm	σ/σ_{320nm}	λ/nm	σ/σ_{320nm}
280	0.145	345	0.548
285	0.224	350	0.411
290	0.328	355	0.292
295	0.454	360	0.196
300	0.594	365	0.124
305	0.735	370	0.075
310	0.862	375	0.043
315	0.954	380	0.023
320	1.000	385	0.012
325	0.991	390	0.006
330	0.929	395	0.003
335	0.824	400	0.001
340	0.691		

Quantum Yields

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

Comments on Preferred Values

The only reported study of the UV absorption spectrum of CH_3CH_2CHOO was obtained by Liu et al. (2014) using the UV photo-dissociation action spectrum technique. CH_3CH_2CHOO can exist in two (stable) conformers, *Z*- and *E*-. The *Z*- form is lower in energy and is expected to be prevalent from the source chemistry employed.

The results show a Gaussian band peaking at 322 nm with no resolved structure, which is attributed to the $\tilde{B}$ $(1A') \leftarrow \tilde{X}(1A')$ electronic transition in CH_3CH_2CHOO. No results have been reported for CH_3CH_2CHOO using conventional absorption spectroscopy. The results from the UV action spectra of Criegee intermediates reported by the University of Pennsylvania group (e.g. CH_2OO, CH_3CHOO, and $(CH_3)_2COO$, Beames et al, 2012; 2013 and Liu et al., 2014) are 2-4 times more intense than spectra recorded using conventional absorption spectroscopy (e.g. Sheps, 2013; Sheps et al., 2013; Ting et al, 2014; Smith et al., 2014) and the IUPAC recommendations. Causes for this discrepancy remain unclear, as discussed in Ting et al. (2014) and Chang et al. (2016). The maximum absorption for CH_3CH_2CHOO reported by Liu et al. (2014) of $\sigma_{322nm} \sim 3.5 \times 10^{-17}$ cm^2 molecule^{-1} is approximately a factor of 3 larger than the IUPAC recommended peak absorption for CH_3CHOO. However, theoretical work indicates that elongation of the alkyl radical in RCHOO Criegee intermediates should not lead to substantial changes in the peak wavelength or intensity of their UV spectra (Yin and Takahashi, 2018).

It is likely that there were errors in the calibration procedures and the absorption cross sections reported by Liu et al. (2014) for CH_3CH_2CHOO are approximately a factor of 2-4 too high. The shape of the spectrum is deemed reliable. The relative cross-sections recommended in the table above were obtained from a Gaussian fit to the experimental data for the range 285 - 366 nm extracted from Figure 3 of the paper by Liu et al. (2014) which gives $\sigma(\lambda) = 3500 \times 10^{-20} \exp(-0.5 \times ((\lambda - 321.7)/21.2)^2)$.

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, (2014), where they were detected by 1+1′ resonance enhanced multiphoton ionization. The HO yield observed with CH_3CH_2CHOO is 10-fold larger than that from CH_2OO, and is greater than from prior studies of OH generation from ozonolysis of E-3-hexene (Kroll et al, 2002).

References

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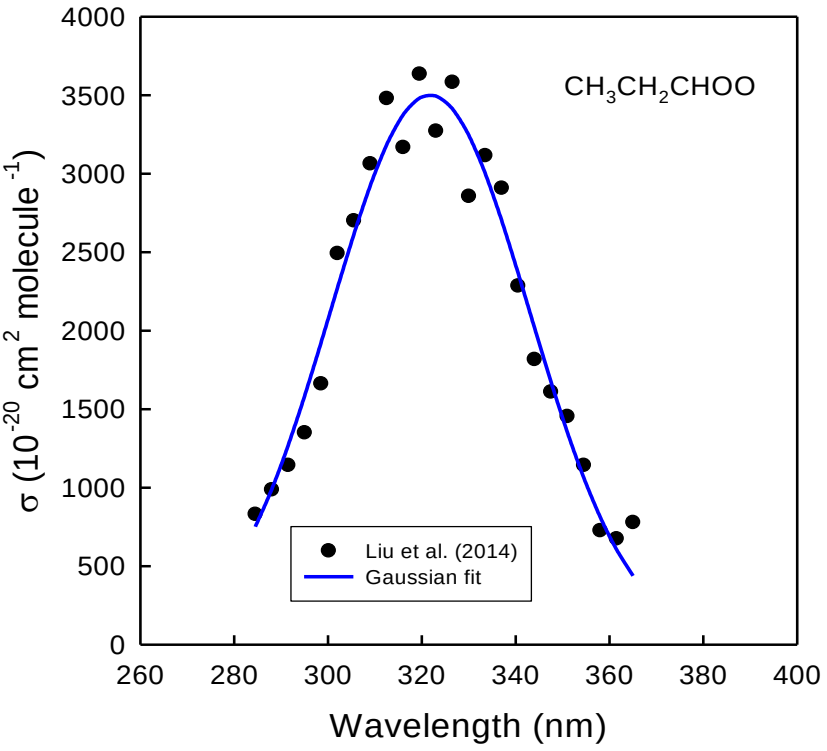

Absorption spectrum of CH_3CH_2CHOO, *Z*- and *E*- conformers not resolved, from Liu et al. (2014) with Gaussian fit.