IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P36
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This datasheet last evaluated: June 2015; last change in preferred values: June 2015.

CH_3CH_2CHOO + hν → products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
CH_3CH_2COO + hυ → CH_3CH_2CO + O(^{3}P) (1)	185	645
→ CH_3CH_2CO + O(^{1}D) (2)	292	410

Absorption cross-section data

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

Comments

(a) Propionaldehyde oxide CH_3CH_2COO, was prepared by PLP (248 nm) of $(CH_3)_2CI_2$ 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 photo-ionisation signal resulting from excitation of the B ← X transition in ground state CH_3CH_2COO 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 $\sim 3.5 \times 10^{-17}$ 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_2COO is similar to that reported recently for CH_3CHOO.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	σ/cm^{-2} x 10^{-20}	λ/nm	σ/cm^{-2} x 10^{-20}
280	341.7	350	1549
285	562.8	355	1099
290	872.9	360	734.1
295	1275	365	461.8
300	1753	370	273.5
305	2270	375	152.5
310	2767	380	80.11
315	3177	385	39.61
320	3434	390	18.44
325	3496	395	8.086
330	3350	400	3.338
335	3024	405	1.298
340	2569	410	0.4750
345	2094	415	0.1637

$\sigma = (3.5 \pm 2) \times 10^{-17}$ cm^2 at λ_{max} (324 nm) ;

Gaussian fit parameters to data of Liu et al. (2014): $\sigma(\lambda) = 3.5 \times 10^{-17} \exp(-0.00120325 \times (324.0 - \lambda)^2)$

Quantum Yields

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

Comments on Preferred Values

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

The results show a Gaussian band peaking at 324 nm with no resolved structure, which is attributed to the in the $\tilde{B}$ (1A′) ← $\tilde{X}$(1A′) electronic transition in CH_3CH_2CHOO. No results have been reported to date for the CH_3CH_2CHOO 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_2OO and CH_3CHOO, Beames et al, (2012) and 2013), differs substantially from spectra recorded subsequently using conventional absorption spectroscopy (e.g. Sheps ,2013; Sheps et al.,2013; Ting et al, 2014; Smith et al., 2014). Causes for this discrepancy remain unclear, as discussed in Ting et al., 2014 and Smith et al, 2014. The weight of evidence favours the spectral shape and cross-sections determined by UV absorption, and 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 CH_3CH_2CHOO 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 above table are obtained from the Gaussian fit to the experimental data. The best estimate for absolute values of 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, (2014), where they were detected by 1+1′ resonance enhanced multiphoton ionization. The OH 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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UV Spectrum - CH

(Liu et al., 20

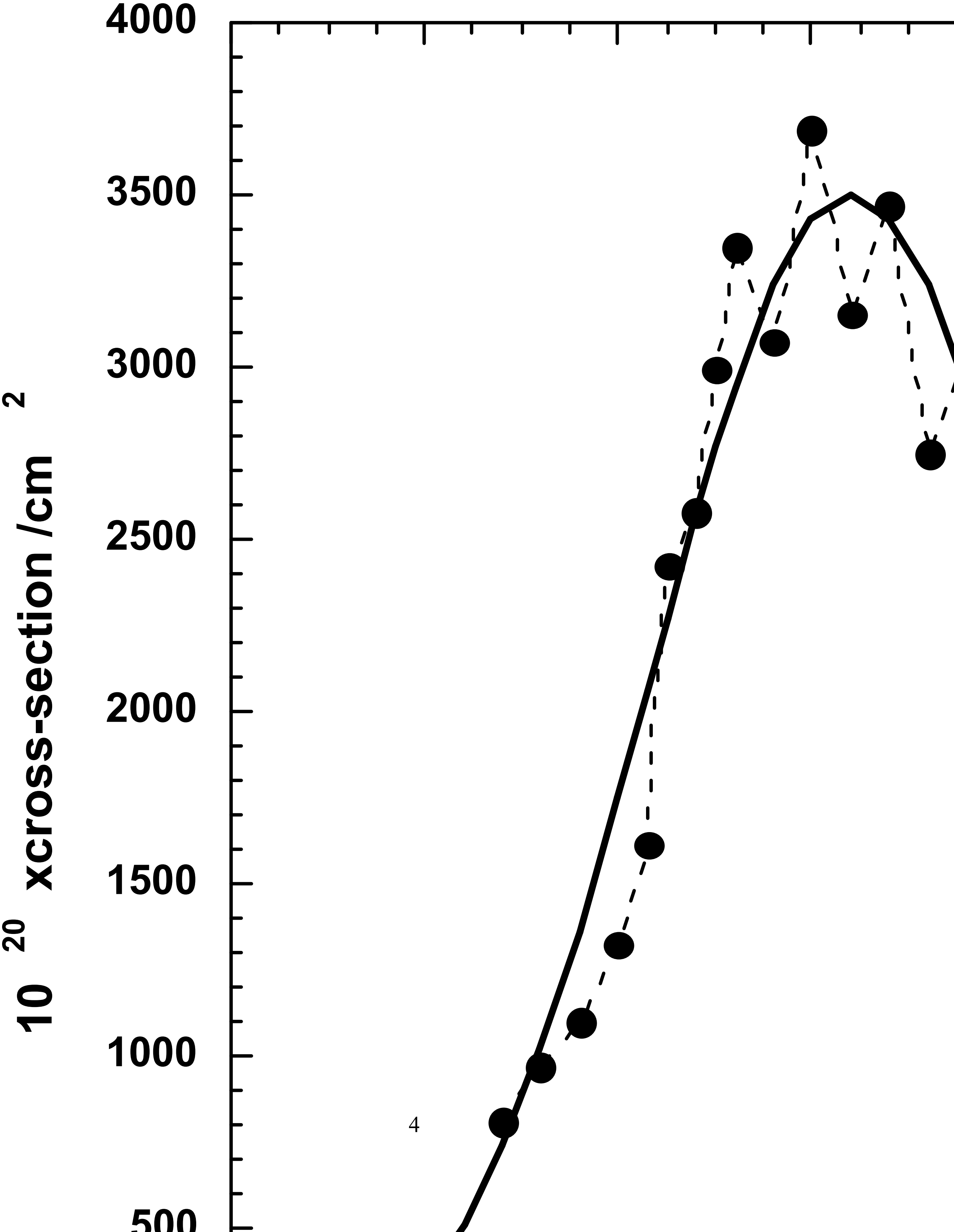

Figure 1: Absorption spectrum of CH_3CH_2CHOO, *syn*- and *anti*- conformers not resolved; Gaussian fit to experimental data from Liu et al., 2014 shown as full line.
lines.