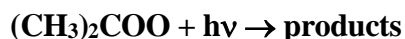


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, Data Sheet P35

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### Primary photochemical transitions

Reaction	
$(\text{CH}_3)_2\text{COO} + h\nu \rightarrow (\text{CH}_3)_2\text{CO} + \text{O}({}^3\text{P})$	(1)
$\rightarrow (\text{CH}_3)_2\text{CO} + \text{O}({}^1\text{D})$	(2)

### Absorption cross-section data

Wavelength range/nm	Reference	Comments
280 – 410	Liu et al., 2014	(a)
280 – 420	Huang et al., 2015	(b)
308 – 352	Chang et al., 2016	(c)
355	Chhantyal-Pun et al., 2017	(d)

### Comments

- (a)  $(\text{CH}_3)_2\text{COO}$  was prepared by PLP (248 nm) of 2,2-diiodopropane,  $(\text{CH}_3)_2\text{CI}_2$  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 118 nm. The UV absorption spectrum was determined from depletion of the  $m/z = 74$  photo-ionisation 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.
- (b)  $(\text{CH}_3)_2\text{COO}$  was generated from pulsed photolysis of a flowing gaseous mixture consisting of  $(\text{CH}_3)_2\text{CI}_2$ ,  $\text{O}_2$ , and buffer gas ( $\text{N}_2$ ) at 248 nm via the reactions:  $(\text{CH}_3)_2\text{CI}_2 + h\nu \rightarrow (\text{CH}_3)_2\text{CI} + \text{I}$ ;  $(\text{CH}_3)_2\text{CI} + \text{O}_2 \rightarrow (\text{CH}_3)_2\text{COO} + \text{IO}$ . Time-resolved difference absorption spectra were recorded and corrected for absorption changes due to precursor and other products (e.g. IO) molecules, leaving a residual absorption attributable to  $(\text{CH}_3)_2\text{COO}$ .
- (c) The absolute absorption cross sections of  $(\text{CH}_3)_2\text{COO}$  under a jet-cooled condition were measured via laser depletion to be  $(1.32 \pm 0.10) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$  at 308 nm and  $(9.6 \pm 0.8) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  at 352 nm. Absolute calibration was achieved using laser beam profiling measurements. Control experiments using  $\text{CH}_2\text{I}_2$  gave an absorption cross section at 308 nm in good agreement with the well-established literature value. The peak UV cross section of  $(\text{CH}_3)_2\text{COO}$  is estimated to be  $(1.75 \pm 0.14) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$  at 330 nm by scaling the UV spectrum of  $(\text{CH}_3)_2\text{COO}$  (Huang et al., 2015; note b) to the absolute cross section at 308 nm.

- (d)  $(\text{CH}_3)_2\text{COO}$  was formed by laser photolysis of 2,2-diiodopropane in the presence of  $\text{O}_2$  and characterized by synchrotron photoionization mass spectrometry and also by cavity ringdown ultraviolet absorption spectroscopy. Cavity ringdown measurements of the acetone oxide removal without added reagents display a combination of first- and second-order decay kinetics, which were deconvolved to derive rate coefficients for both unimolecular thermal decay,  $k_{\text{dec}}$  (see CGI\_14), and the self-reaction of  $(\text{CH}_3)_2\text{COO}$ . The loss of  $(\text{CH}_3)_2\text{Cl}_2$  following photodissociation was used to calibrate the initial  $(\text{CH}_3)_2\text{COO}$  concentration and determine  $\sigma(355\text{nm}) = (1.45 \pm 0.24) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$  and the  $(\text{CH}_3)_2\text{COO}$  self-reaction rate coefficient,  $k = (6.0 \pm 1.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

## Preferred Values

### Absorption cross-sections at 298 K

$\lambda/\text{nm}$	$10^{20} \sigma/(\text{cm}^2 \text{ molecule}^{-1})$	$\lambda/\text{nm}$	$10^{20} \sigma/(\text{cm}^2 \text{ molecule}^{-1})$
280	279	345	1355
285	403	350	1146
290	560	355	929
295	747	360	723
300	955	365	540
305	1171	370	387
310	1379	375	266
315	1557	380	175
320	1687	385	111
325	1754	390	67
330	1750	395	39
335	1675	400	22
340	1538	405	12

$\sigma = (1.75 \pm 0.53) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$  at  $\lambda_{\text{max}}(330 \text{ nm})$ ;

Gaussian fit parameters to extracted data from the absorption spectrum for the range 280 - 390 nm reported by Chang et al. (2016):  $\sigma(\lambda) = 1747 \times 10^{-20} \exp(-0.5 \times ((\lambda - 327.2)/24.58)^2)$

## Quantum Yields

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

### Comments on Preferred Values

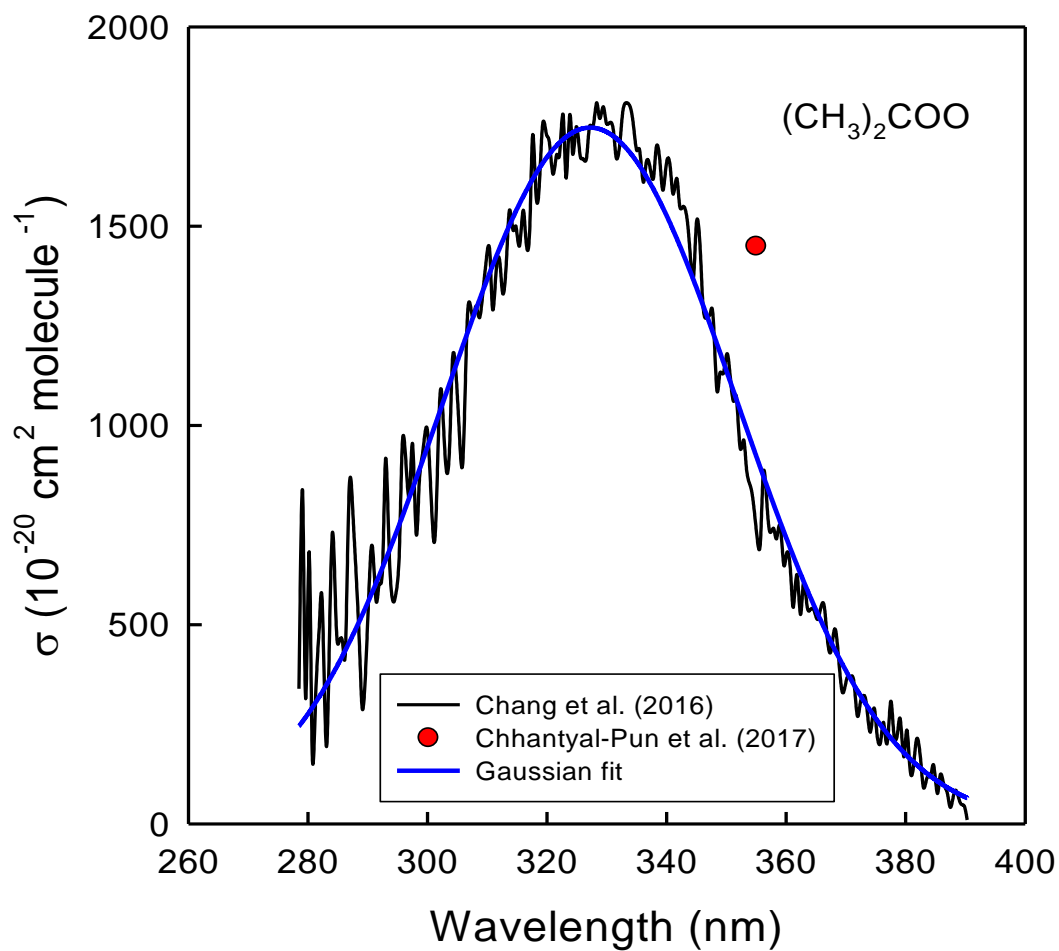
The first UV absorption spectrum of  $(\text{CH}_3)_2\text{COO}$  was reported by Liu et al. (2014), using UV photo-dissociation action technique. The results show a Gaussian band peaking at 330 nm with no resolved structure, which is attributed to the  $\tilde{\text{B}}(1\text{A}') \leftarrow \tilde{\text{X}}(1\text{A}')$  electronic transition. Huang et al. (2015) used conventional absorption spectroscopy and reported a spectrum for  $(\text{CH}_3)_2\text{COO}$  slightly broader than the jet-cooled spectrum reported by Liu et al. (2014). The contribution of hot bands in the room-temperature spectrum would cause broadening in comparison with the low-temperature spectrum of Liu et al. (2014). The results from the UV action spectra of several Criegee intermediates reported by the University of Pennsylvania group (e.g.  $\text{CH}_2\text{OO}$  and  $\text{CH}_3\text{CHOO}$ , Beames et al., 2012; 2013) differ substantially from spectra recorded subsequently using conventional

absorption spectroscopy (e.g. Sheps, 2013; Ting et al, 2014; Smith et al., 2014). The absorption bands determined using photo-dissociation action spectroscopy by the University of Pennsylvania group are narrower, peak at a shorter wavelength, and the cross sections are up to a factor of 4 higher than those measured 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 Chang et al. (2016). The latter study included control experiments which reproduced the well-established absorption cross section for  $\text{CH}_2\text{I}_2$  at 308 nm. The weight of evidence favours the spectral shape and cross-sections determined by UV absorption and the recommended  $(\text{CH}_3)_2\text{COO}$  spectrum is based upon the work of Huang et al. (2015) and Chang et al. (2016). The figure below shows the experimental values reported by Chang et al. (2014) and a Gaussian fit to those data. The cross-sections listed in the table of preferred values are obtained from the Gaussian fit to the experimental data and are estimated to have an uncertainty of  $\pm 30\%$ . 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 HO yield observed with  $\text{CH}_3\text{CHOO}$  is 6-fold larger than that from  $\text{CH}_2\text{OO}$ , consistent with prior studies of HO generation from alkene ozonolysis (Kroll et al., 2002).

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Absorption spectrum of  $(\text{CH}_3)_2\text{COO}$ ; full line is Gaussian fit to experimental data (filled circles) from Chang et al. (2016). Gaussian fit parameters to data for  $(\text{CH}_3)_2\text{COO}$ :  $\sigma(\lambda) = 1747 \times 10^{-20} \exp(-0.5 \times ((\lambda - 327.2)/24.58)^2)$