IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P38

This datasheet last evaluated: May 2020; last change in preferred values: May 2020.

$(CH=CH_2)(CH_3)COO$ (*Z*- and *E*-) + hν → products

Primary photochemical transitions

Reaction
$(CH=CH_2)(CH_3)COO + h\upsilon \rightarrow (CH_2=CH)(CH_3)COO + O(^3P)$ (1) $\rightarrow (CH_2=CH)(CH_3)COO + O(^1D)$ (2)

Absorption cross-section data

Wavelength range/nm	Reference	Comments
305-480	Vansco et al., 2018	(a)

Comments

(a) Methyl vinyl ketone oxide, $(CH=CH_2)(CH_3)COO$, was prepared by PLP (248 nm) of (*Z*-/*E*)-1,3-diiodobut-2-ene 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* = 86 photo-ionisation signal resulting from excitation of the $\Pi^* \leftarrow \Pi$ transition of ground state $(CH=CH_2)(CH_3)COO$ molecules by tunable UV radiation (305 – 480 nm). The UV-induced depletion increased linearly with UV power and a peak absorption cross section at 388 nm of the order of 10^{-17} cm^2 molecule^{-1} was estimated.

Preferred Values

Absorption cross-sections at 298 K relative to value at 388 nm

λ/nm	σ/σ_{388nm}	λ/nm	σ/σ_{388nm}
310	0.230	390	0.977
320	0.308	400	0.722
330	0.380	410	0.528
340	0.454	420	0.349
350	0.525	430	0.219
360	0.578	440	0.122
370	0.655	450	0.059
380	0.816		
388	1.000		

Quantum Yields

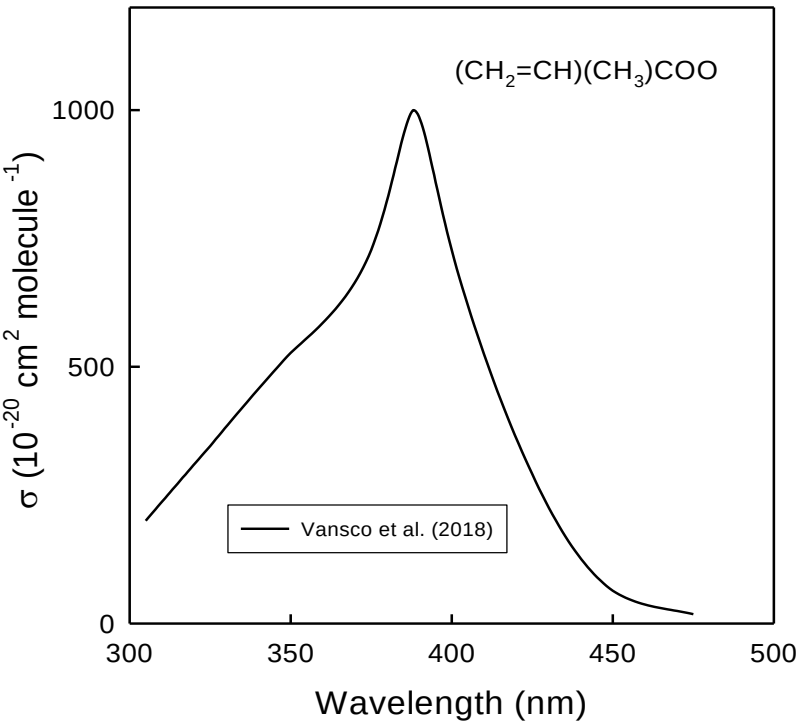
ϕ_1 = 1.0 for 305 < λ <430 nm.

Comments on Preferred Values

The only reported study of UV absorption spectrum of the methyl vinyl ketone oxide Criegee intermediate, $(CH=CH_2)(CH_3)COO$, was obtained by Vansco et al. (2018). The UV photo-dissociation action spectrum technique was used to record the spectrum of a mixture of the four conformers of $(CH=CH_2)(CH_3)COO$ (i.e. two rotamers of each of *Z*- and *E*-$(CH=CH_2)(CH_3)COO$). The spectrum in the range 305-425 nm was broad and unstructured with a maximum at 388 nm which was roughly estimated to be of the order of 10^{-17} cm^2 $molecule^{-1}$. In light of the rough estimate, no recommendation is given for the absolute absorption cross sections but the shape of the spectrum is indicated in the table above. Absorption at λ < 430 nm leads to rapid dissociation to methyl vinyl ketone and $O(^1D)$ which were detected using 2 + 1 REMPI. The photodissociation quantum yields are likely to be close to unity.

References

Vansco, M. F., Marchetti, B., Lester, M. I.: J. Chem. Phys., 149, 244309, 2018.



Absorption spectrum of $(CH_2=CH)(CH_3)COO$, *Z*- and *E*- conformers not resolved, from Figure 6 in Vansco et al. (2018).