IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P39

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

$(C(CH_3)=CH_2)CHOO$ (*Z*- and *E*-) + hν → products

Primary photochemical transitions

Reaction	
$(C(CH_3)=CH_2)CHOO + h\upsilon$	$\rightarrow CH_2=C(CH_3)CHO + O(^3P)$ (1) $\rightarrow CH_2=C(CH_3)CHO + O(^1D)$ (2)

Absorption cross-section data

Wavelength range/nm	Reference	Comments
315-500	Vansco et al., 2019	(a)

Comments

(a) Methacrolein oxide, $(C(CH_3)=CH_2)CHOO$, 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 $(C(CH_3)=CH_2)CHOO$ molecules by tunable UV radiation (305 – 480 nm). The UV-induced depletion increased linearly with UV power and an absorption cross section at 380 nm of approximately 3×10^{-18} cm^2 molecule^{-1} was estimated.

Preferred Values

Absorption cross-sections at 298 K relative to value at 380 nm

λ/nm	σ/σ_{380nm}	λ/nm	σ/σ_{380nm}
320	0.886	410	0.823
330	0.850	420	0.759
340	0.749	430	0.672
350	0.749	440	0.471
360	0.886	450	0.466
370	0.938	460	0.270
380	1.000	470	0.249
390	0.957	480	0.170
400	0.883	490	0.098

Quantum Yields

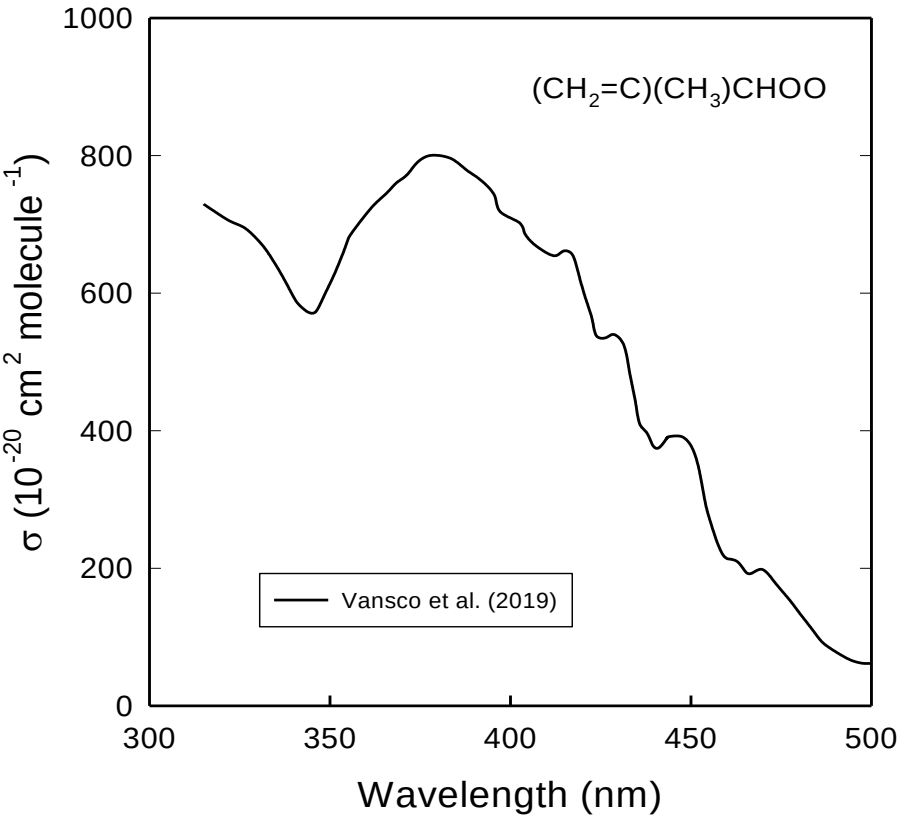
ϕ_1 = 1.0 for 315 < λ <500 nm.

Comments on Preferred Values

The only reported study of UV absorption spectrum of the methacrolein oxide Criegee intermediate, ($C(CH_3)=CH_2$)CHOO, was obtained by Vansco et al. (2019). The UV photo-dissociation action spectrum technique was used to record the spectrum of a mixture of the four conformers of ($C(CH_3)=CH_2$)CHOO (i.e. two rotamers of each of *Z*- and *E*-($C(CH_3)=CH_2$)CHOO). The spectrum in the range 315-500 nm was broad with structured at wavelengths > 400 nm with a maximum at 380 nm which was estimated to be approximately 3×10^{-18} 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 < 500 nm leads to rapid dissociation to methacrolein and $O(^1D)$ atoms which were detected using 2 + 1 REMPI. The photodissociation quantum yields are likely to be close to unity.

References

Vansco, M. F., Marchetti, B., Trongsiriwat, N., Bhagde, T., Wang, G., Walsh, P. J., Klippenstein, S. J., Lester, M. I.: J. Am. Chem. Soc., 141, 15058, 2019.



Absorption spectrum of ($C(CH_3)=CH_2$)CHOO, *Z*- and *E*- conformers not resolved, from Figure 4 in Vansco et al. (2019).