IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, Data Sheet P40

The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (http://iupac.pole-ether.fr)
This datasheet last evaluated: Sep. 2020; last change in preferred values: Sep. 2020.

$CH_3C(O)OOH + h\nu \rightarrow HO + CH_3C(O)O$

Primary photochemical transitions

Reaction	ΔH /kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3C(O)OOH + h\upsilon \rightarrow CH_3C(O)O + HO$		661

Absorption cross-section data

Wavelength range/nm	Reference	Comments
210 – 340	Orlando and Tyndall, 2003	(a)

Comments

(a) Absorption of light (D_2-Lamp) over 90 cm path-length at a spectral resolution of 0.6 nm (0.3 m monochromator with diode array detector). FTIR analysis showed that the gas-phase $CH_3C(O)OOH$ sample (0.08 – 1 Torr, obtained from the headspace of 32 wt.% liquid samples in acetic acid) contained 60-70 wt.% $CH_3C(O)OOH$, ~15% $CH_3C(O)OH$ and ~15% H_2O. A contribution from H_2O_2 was ruled out as it is expected to be rapidly converted to H_2O in the apparatus used.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\,\sigma$ (cm^2 molecule^{-1})	λ/nm	$10^{20}\,\sigma$ (cm^2 molecule^{-1})	λ/nm	$10^{20}\,\sigma$ (cm^2 molecule^{-1})
210	38.1	254	2.42	298	0.141
212	33.1	256	2.16	300	0.123
214	29.5	258	1.93	302	0.1
216	25.4	260	1.71	304	0.094
218	21.7	262	1.53	306	0.078
220	18.9	264	1.35	308	0.069
222	16	266	1.21	310	0.062
224	13.9	268	1.06	312	0.045
226	12	270	0.945	314	0.044
228	10.5	272	0.835	316	0.04
230	9.1	274	0.742	318	0.035
232	8.01	276	0.651	320	0.025
234	7.03	278	0.574	322	0.02

236	6.31	280	0.506	324	0.02
238	5.61	282	0.444	326	0.017
240	5.03	284	0.386	328	0.014
242	4.83	286	0.334	330	0.009
244	4.31	288	0.297	332	0.011
246	3.82	290	0.256	334	0.011
248	3.41	292	0.226	336	0.009
250	3.05	294	0.193	338	0.009
252	2.71	296	0.17	340	0.006

Quantum Yields

$\phi_1 = 1.0$ for $280 < \lambda < 340$ nm.

Comments on Preferred Values

The only reported gas-phase spectrum of $CH_3C(O)OOH$ is that of Orlando and Tyndall (2003), who also analysed impurities using FTIR. They reported uncertainties of ±10% at $\lambda < 290$ nm, ±20% at 320 nm and about ±50% at 330 nm. The absorption spectrum resembles those of other organic peroxides and H_2O_2 (see e.g. datasheets PHOx2, and P12). Orlando and Tyndall (2003) indicate that the absorption cross-sections fall-off more rapidly with wavelength at 248 K than at 298 K, but were unable to quantify the temperature dependence of the cross-sections.

The 240 and 266 mn photo-dissociation of $CH_3C(O)OOH$ under collision free conditions results in the formation of ground state HO, with no vibrational excitation and the acetyloxy co-fragment ($CH_3C(O)O$) dissociates rapidly to $CH_3 + CO_2$ (Keller et al, 2008). The overall quantum yield of dissociation of $CH_3C(O)OOH$ has not been determined experimentally, though given the spectral similarity to other peroxides, a unity quantum yield for HO formation is expected at wavelengths between 240 and 340 nm where absorption is due to a peroxy $n \rightarrow \pi^*$ transition.

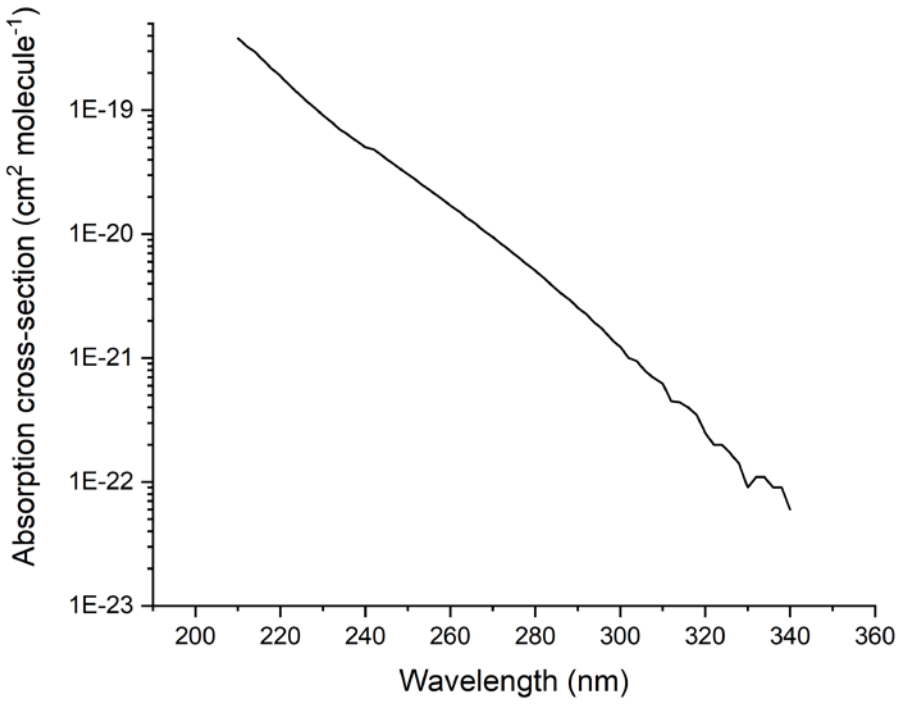
As there is only one study of the UV spectrum of $CH_3C(O)OOH$ and poor agreement in the published infra-red absorption spectra of $CH_3C(O)OOH$ (Berasategui, 2020) we extend the uncertainty (by a further factor two at all wavelengths) and highlight the requirement for further laboratory and theoroetical investigation, including determination of the absorption cross-sections at lower temperatures and the photodissociation quantum yield.

References

Berasategui, M., Amedro, D., Vereecken, L., Lelieveld, J., and Crowley, J. N., Atmos. Chem. Phys. Discuss., 2020, 1-29, 2020.

Keller, B. K., Wojcik, M. D., and Fletcher, T. R., J. Photochem. Photobiol. A-Chem., 195, 10-22, 2008.

Orlando, J. J., and Tyndall, G. S., J. Photochem. Photobiol. A-Chem., 157, 161-166, 2003.



UV absorption cross sections of $CH_3C(O)OOH$ reported by Orlando and Tyndall, 2003.