

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, Data Sheet P37

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### CH<sub>3</sub>C(O)C(O)OH + hν → products

#### Primary photochemical processes

Reaction		ΔH / kJ·mol <sup>-1</sup> *	λ <sub>threshold</sub> /nm
CH <sub>3</sub> C(O)C(O)OH + hν → CH <sub>3</sub> CHO + CO <sub>2</sub>	(1)	-28	--
→ CH <sub>3</sub> C(O)OH + CO	(2)	-12	--
→ CH <sub>3</sub> CO + HOCO	(3)	301	397
→ CH <sub>3</sub> CO + CO + OH	(4)	448	267

\* ΔH<sub>f</sub> (CH<sub>3</sub>C(O)C(O)OH) taken from Tyndall et al. (2001).

#### Preferred Values

#### Absorption cross-sections (σ) for CH<sub>3</sub>C(O)C(O)OH at 298 K

λ (nm)	σ (10 <sup>-20</sup> cm <sup>2</sup> )	λ (nm)	σ (10 <sup>-20</sup> cm <sup>2</sup> )	λ (nm)	σ (10 <sup>-20</sup> cm <sup>2</sup> )
253	1.572	303	0.6340	353	4.055
255	1.544	305	0.7567	355	3.700
257	1.396	307	0.8965	357	3.194
259	1.074	309	1.031	359	2.941
261	0.8076	311	1.157	361	3.152
263	0.7217	313	1.272	363	2.713
265	0.6927	315	1.427	365	2.524
267	0.5654	317	1.673	367	2.540
269	0.3662	319	1.907	369	3.038
271	0.2292	321	2.143	371	2.338
273	0.1849	323	2.290	373	1.599
275	0.1857	325	2.411	375	1.099
277	0.1781	327	2.560	377	0.8105
279	0.1381	329	2.748	379	0.5122
281	0.1031	331	3.068	381	0.2427
283	0.09958	333	3.450	383	0.1457
285	0.1154	335	3.574	385	0.1004
287	0.1403	337	3.616	387	0.07470
289	0.1715	339	3.539	389	0.05679
291	0.2112	341	3.529	391	0.03804
293	0.2604	343	3.740	393	0.02303
295	0.3205	345	3.782	395	0.01127
297	0.3865	347	4.117	397	0.003924
299	0.4557	349	4.336	399	
301	0.5319	351	4.291	401	

The cross sections listed are 2 nm averages centred around the listed wavelength.

## Quantum yields for CH<sub>3</sub>C(O)C(O)OH photolysis

$$\phi (290 < \lambda < 390 \text{ nm, 1 bar air, 298 K}) = \phi_1 + \phi_2 + \phi_3 + \phi_4 = 0.20 \pm 0.1$$

$$\phi (290 < \lambda < 390 \text{ nm, M, 298 K}) = 0.81 \times ((3.089 \times 10^{-17} \text{ M} + 204.9)) / (1.09 \times 10^{-37} \text{ M}^2 + 1.566 \times 10^{-16} \text{ M} + 165.3)$$

$$\phi_1 = (0.6 \pm 0.1) \times \phi$$

$$\phi_2 = (0.05 \pm 0.05) \times \phi$$

$$\phi_3 = (0.35 \pm 0.1) \times \phi$$

### *Comments on Preferred Values*

#### *Absorption cross-sections.*

The absorption cross-sections listed in the table above were taken by averaging (2nm intervals) over the cross-sections (measured at 0.066 nm resolution) from the work of Horowitz et al. (2001). Agreement between the more detailed studies of Horowitz et al. (2001) and Mellouki and Mu (2003) is poor, especially at wavelengths shorter than ~ 310 nm where the cross-sections of Mellouki and Mu (2003) are up to a factor two larger. In the actinically important region between 310 and 375 nm, the cross-sections of Mellouki and Mu (2003) are 20-30 % larger.

The differences may, in part, be attributed to problems handling pyruvic acid, which has a low vapour pressure and tends to condense on surfaces. In order to reduce artefacts in spectral shape due to condensation of pyruvic acid on the optical windows of their set-up, Horowitz et al. (2001) heated the windows to 60 °C. For this reason and because of their extended wavelength range we prefer their data. Once normalised to a cross section of  $3.82 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$  at 350 nm (as reported in a personal communication to Berges and Warneck (1992)) the 340 K absorption spectrum of Yamamoto et al. (1985) is in good agreement with Horowitz et al. (2001) in terms of cross-sections between 310 and 390 nm, though appears to be shifted in wavelength (to the red) by ~ 3nm.

#### *Quantum yield and products ( $\lambda > 290\text{nm}$ )*

There have been several studies of the photo-dissociation of pyruvic acid, at different pressures, temperatures and discrete wavelengths. Under all conditions relevant for the lower atmosphere, the major products observed are CO<sub>2</sub> and acetaldehyde. These are formed (R1) via exothermic decarboxylation involving a 5-membered transition state that decomposes to CO<sub>2</sub> and methylhydroxycarbene, the latter rearranging to acetaldehyde, which involves tunnelling through a substantial barrier (Schreiner et al., 2011). Other (minor) stable products observed in air are HCHO, CH<sub>4</sub>, CH<sub>3</sub>OH, CO and CH<sub>3</sub>C(O)OH. CO and CH<sub>3</sub>C(O)OH may be formed directly via isomerisation of pyruvic acid to a  $\alpha$ -lactone that dissociates to CH<sub>3</sub>C(O)OH and CO (R2) (Da Silva, 2016) or secondary processes following formation of the CH<sub>3</sub>CO and HOCO radicals in (R3) (Reed Harris et al., 2016; Berges and Warneck, 1992). Experiments at 355 nm (Mellouki and Mu, 2003) identified OH as a direct photolysis product at a yield of  $0.05 \pm 0.03$  in 100-300 Torr He or up to 50 Torr N<sub>2</sub>. The authors propose its formation in reaction (R4), though at 355 nm this channel appears to be energetically disfavoured and the origin of OH in this experiment remains unexplained.

The formation of CO<sub>2</sub> and acetaldehyde products upon photolysis of pyruvic acid at 366 nm (at 80-85 °C, 5 Torr) was first documented by Vesley and Leermakers (1964), who derived a photolysis quantum yield and yield of CO<sub>2</sub> close to unity, with CH<sub>3</sub>CHO formed at 60-65 % yield. Small amounts of CO and CH<sub>4</sub> were also observed. Addition of N<sub>2</sub> or O<sub>2</sub> bath gas (both at 50 Torr) did not affect the yields of CO<sub>2</sub> or acetaldehyde. Yamamoto et al. (1985) also report a near-unity yield of CO<sub>2</sub> under similar conditions and at the same wavelength (366 nm). CO<sub>2</sub> and acetaldehyde were the only products found at 320, 245 and 366 nm, with the acetaldehyde-to-

CO<sub>2</sub> ratio varying according to reaction conditions and reducing to ~0.1 in 150 Torr of air, whereby the absolute yield of CO<sub>2</sub> remained constant. In accordance with these studies, Berges and Warneck, (1992) also found CO<sub>2</sub> and CH<sub>3</sub>CHO to be the major products formed in pyruvic acid photolysis at 350 nm under atmospheric conditions (1 bar air), with yields of  $1.27 \pm 0.18$  and  $0.48 \pm 0.01$ , respectively. Acetic acid was additionally identified, with a yield of 0.14 and the addition of NO<sub>2</sub> resulted in formation of CH<sub>3</sub>C(O)O<sub>2</sub>NO<sub>2</sub> indicating that acetyl radicals were formed during photolysis. The average photolysis quantum yield derived by Berges and Warneck (1992) was  $0.85 \pm 0.16$  at a pressure of 600 Torr air. The use of the presently preferred, larger cross-section at 350 nm ( $4.47 \times 10^{-20}$  cm<sup>2</sup> molecule<sup>-1</sup>) rather than the value of  $3.82 \times 10^{-20}$  cm<sup>2</sup> molecule<sup>-1</sup> which they used would reduce the photolysis quantum yield to  $0.73 \pm 0.14$ .

Reed Harris et al. (2016) carried out a systematic study of pyruvic acid photolysis using a solar-matched, broad-band UV source ( $\lambda > 290$  nm) and at different pressures of air or N<sub>2</sub>. They found the photolysis quantum yields depended strongly on pressure with values greater than unity at zero pressure, decreasing to about 0.2 at 600 Torr air. Use of the presently recommended absorption cross sections rather than a recommended average (Sander et al. 2011) of those reported by Mellouki and Mu (2003) and Horowitz et al. (2001) would increase their quantum yields by  $\approx 10$  %. In these experiments, the quantum yields measured in air were slightly lower than those obtained in N<sub>2</sub> and a Stern-Volmer analysis of the data indicated that both singlet and triplet states are involved in the dissociation of pyruvic acid with collisional quenching of the first excited singlet state by nitrogen and quenching of both singlet and triplet states in air. The small difference in quantum yields when using nitrogen or air as bath gas was taken to indicate that photo-dissociation occurs mainly from the singlet state, consistent with previous observations of a negligible or weak effect when adding O<sub>2</sub>. However, it is not obvious to what extent the lower quantum yields in air are related to changes in secondary processes when O<sub>2</sub> is present. The pressure dependence observed by Reed Harris et al. (2016) is consistent with experiments in environmental chambers using natural sunlight and at atmospheric pressure of air, which along with identifying CO<sub>2</sub> and CH<sub>3</sub>CHO as dominant end-products, also report quantum yields that are significantly lower than unity (Grosjean, 1983; Calvert et al., 2011). The yield of CH<sub>3</sub>CHO (the major product) was ~60 % with no apparent trend with either total pressure or use of N<sub>2</sub> or air bath-gas.

More recent experiments from the same group (Reed Harris et al., 2017) using lower partial pressures of pyruvic acid resulted in much lower yields of CH<sub>3</sub>CHO (~5% in air) with formation of acetic acid the dominant product ( $63 \pm 12\%$ ). The authors suggest that the low yield of CH<sub>3</sub>CHO in air may be due to reactions of the methylhydroxycarbene with O<sub>2</sub> to form HO<sub>2</sub> and CH<sub>3</sub>C(O)O<sub>2</sub> that compete with rearrangement to CH<sub>3</sub>CHO, the latter being favoured (at high pyruvic acid concentrations) by dimerization (Morais et al., 2015). They also suggest that the photolysis of methylhydroxycarbene may compete with its rearrangement to CH<sub>3</sub>CHO. The carbon balance in the more recent experiments was however very poor ( $\sim 12 \pm 3$  % in N<sub>2</sub>,  $20 \pm 1$  % in air) compared to their previous work (56-98%).

Reed Harris et al (2017) also derived a larger quantum yield for pyruvic acid photolysis in 1 bar air ( $> 3$ ) and in 1 bar N<sub>2</sub> ( $0.84 \pm 0.1$ ) compared to their previous work. The apparently divergent quantum yield results in the two studies are suggested to be tied to the lower pyruvic acid concentrations used in the 2017 study, the larger than unity quantum yield in air stemming from secondary losses of pyruvic acid (potentially involving reactions of the initially formed methylhydroxycarbene).

Several experimental observations support the existence of radical formation in channel (3). The fact that zero-pressure CO<sub>2</sub> quantum yields exceeding unity were derived in several studies is evidence for its formation in secondary processes involving HOCO and CH<sub>3</sub>CO. In air, HOCO will react with O<sub>2</sub> to form HO<sub>2</sub> and CO<sub>2</sub>, whereas CH<sub>3</sub>CO reacts with O<sub>2</sub> to form OH, CO and HCHO at low pressures and the CH<sub>3</sub>C(O)O<sub>2</sub> peroxy radical at high pressures. Reactions of CH<sub>3</sub>C(O)O<sub>2</sub> with itself or with HO<sub>2</sub> result in formation of the minor stable products observed CH<sub>3</sub>C(O)OH, HCHO, CH<sub>3</sub>OH and also OH. The formation of OH may enhance the apparent

photolysis quantum yield by removing pyruvic acid and also change the product yields by reaction with e.g. CH<sub>3</sub>CHO.

#### *Photolysis at other wavelengths*

Dynamics studies of the 193 nm and 248 nm photolysis of pyruvic acid indicate formation of OH and CO<sub>2</sub> (Rosenfeld and Weiner, 1983; O'Neill et al., 1987; Hall et al., 1992; Dhanya et al., 2003). Vibrational excitation of ground state (S<sub>0</sub>) pyruvic acid, either directly via overtone excitation (Takahashi et al., 2008) or following internal conversion from S<sub>1</sub> (Da Silva 2016) is also reported to predominantly lead to formation of CH<sub>3</sub>CHO and CO<sub>2</sub> with high quantum yield.

Our understanding of the primary photochemical processes is still incomplete, and there are inconsistencies within the datasets covering photolysis at actinic wavelengths. The lack of pressure dependence in the near-unity quantum yields measured by Vesley and Leermakers (1964) and Yamamoto et al. (1985) and the high quantum yield at 600 Torr air derived by Berges and Warneck (1992) are incompatible with the strong pressure dependence observed by Reed Harris et al., (2016) and the low quantum yields derived from chamber experiments at 1 bar air. The dependence of the quantum yield on the pyruvic acid and O<sub>2</sub> partial pressure observed by Reed-Harris et al (2017) needs confirmation.

We note that the photo-dissociation of several atmospheric carbonyl species is characterised by significant reduction in quantum yields at high pressures. For the purpose of modelling the photolysis of pyruvic acid in the atmosphere we therefore recommend a pressure dependent quantum yield based on the parameterisation of Reed Harris et al. (2016) and the unpublished chamber studies summarised in Calvert et al. (2011), but with the zero pressure quantum yield reduced to 1.0 (rather than the value of 1.27 they report). The variable yields of CH<sub>3</sub>CHO, CH<sub>3</sub>C(O)OH and CO<sub>2</sub> are roughly consistent with branching ratios of 0.6, 0.05 and 0.35 for (R1), (R2) and (R3), respectively. The uncertainties on the overall photo-dissociation quantum yield and the branching to the three product channels listed are chosen to reflect divergence in experimental datasets and the poorly constrained role of secondary reactions. The likely wavelength dependence of each process is neglected in this parameterisation and more data exploring the temperature, pressure and wavelength dependence of the primary quantum yield and the relative importance of the three accessible decomposition pathways are required to accurately predict the fate of pyruvic acid throughout the lower atmosphere, as is confirmation of the absorption cross-sections.

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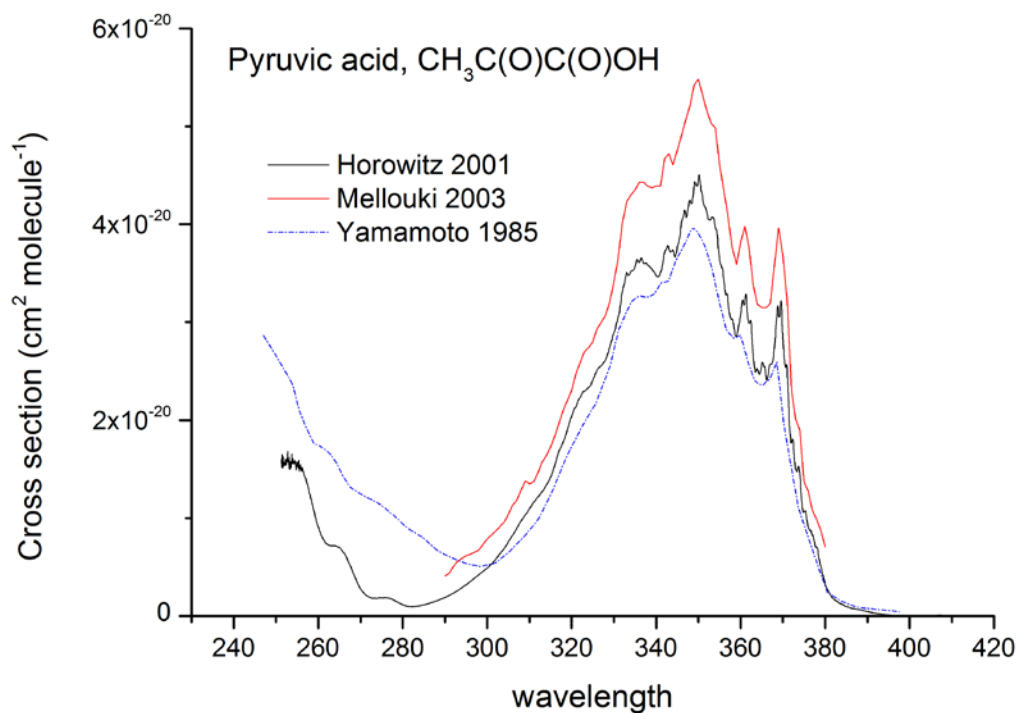
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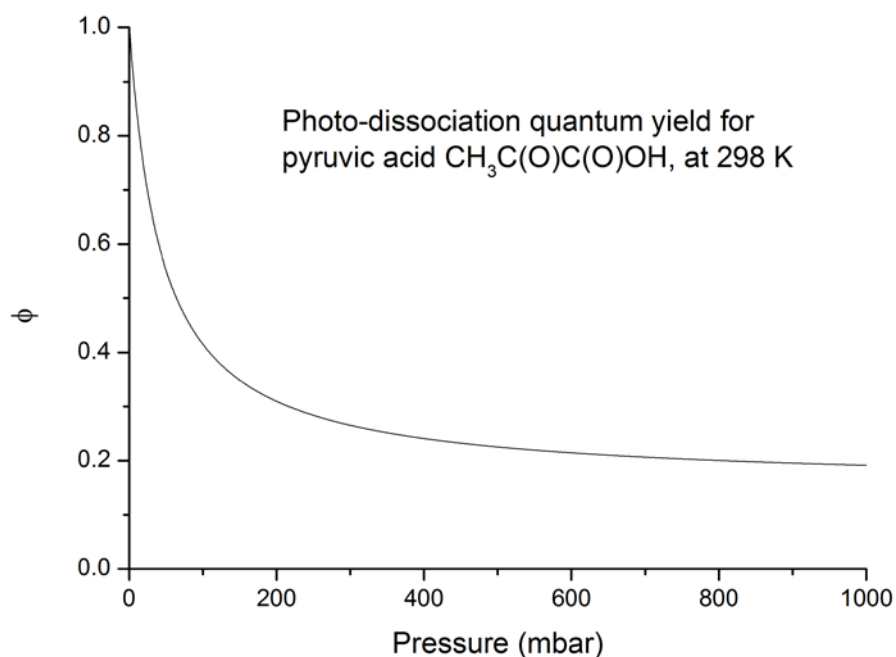
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**Absorption cross sections of pyruvic acid at room temperature:** The data of Yamamoto et al (1985) have been blue-shifted by 3 nm, the dataset of Horowitz et al. (2003) are the preferred values.



**Quantum yields (290-350 nm) for pyruvic acid at room temperature:** The pressure dependence is from Reed Harris et al. (2016), modified to give a yield of unity at zero pressure.