Photochemistry of aqueous pyruvic acid

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The study of organic chemistry in atmospheric aerosols and cloud formation is of interest in predictions of air quality and climate change. It is now known that aqueous phase chemistry is important in the formation of secondary organic aerosols. Here, the photo-reactivity of pyruvic acid (PA; CH₂COCOOH) is investigated in aqueous environments characteristic of atmospheric aerosols. PA is currently used as a proxy for α-dicarboxyls in atmospheric models and is abundant in both the gas phase and the aqueous phase (atmospheric aerosols, fog, and clouds) in the atmosphere. The photo-reactivity of PA in these phases, however, is very different, thus prompting the need for a mechanistic understanding of its reactivity in different environments. Although the decarboxylation of aqueous phase PA through UV excitation has been studied for many years, its mechanism and products remain controversial. In this work, photolysis of aqueous PA is shown to produce acetoin (CH₂CHOHCOCH₂), lactic acid (CH₃CHOHCOOH), acetic acid (CH₃COOH), and oligomers, illustrating the progression from a three-carbon molecule to four-carbon and even six-carbon molecules through direct photolysis. These products are detected using vibrational and electronic spectroscopy, NMR, and MS, and a reaction mechanism is presented accounting for all products detected. The relevance of sunlight-initiated PA chemistry in aqueous environments is then discussed in the context of processes occurring on atmospheric aerosols.

atmospheric chemistry | sunlight-initiated chemistry

Predictive models of air quality and climate change require understanding of the role that organic compounds play in aerosol interactions with radiation (1, 2). Volatile organic compounds in the atmosphere oxidize with the products of this chemistry, contributing to the formation of secondary organic aerosols (SOAs) (3, 4). Current model predictions, however, do not agree with findings of field measurements and highlight the importance of understanding organic reaction mechanisms, which are expected to affect the oxidizing capacity of the atmosphere, the formation of SOAs, and climate-relevant aerosol properties (1–10). Organic polymers have been identified as important contributors to SOAs. These polymeric species do not result from gas phase reactions (11) but rather appear to be products of organic reactions in condensed (aqueous) phase, where high-molecular-weight compounds, polymers, and oligomers can be generated (1, 5, 12–15). Recent results have mainly addressed radical reactions in aqueous environments (5, 7, 16), with only a few using direct photolysis (13, 17). The need for understanding organic reaction mechanisms in aqueous solutions representative of aqueous media in the atmosphere (aerosols, cloud droplets, fog, and rain) has been recognized (1, 2, 7, 18).

In aqueous environments with sufficiently high organic concentrations, polyfunctional carbonyl compounds react to form high-molecular-weight species, polymers, and oligomers, yet the reaction mechanisms responsible for these aqueous phase reactions remain elusive targets for investigation (5, 6, 13, 19–21). This investigation provides fundamental laboratory results and mechanisms for the photochemistry of pyruvic acid (PA) in an aqueous solution. PA, an oxidative product of isoprene, is abundant in the atmosphere in gas and aerosol phases, and it has been used in models as a proxy for atmospheric α-dicarboxyls (3, 22–24). PA undergoes decarboxylation in the gas and aqueous phases by means of different mechanisms. Decarboxylation of gas phase PA has been seen to occur thermochemically, through IR multi-photon pyrolysis, as well as through UV and visible excitation (13, 25–36). The main removal pathway of gas phase PA from the troposphere is UV photolysis, with reaction with OH radical providing a minor contribution (31). The photochemistry (direct photolysis) of PA in an aqueous solution remains controversial in the literature, and it is the focus of the present laboratory study.

Photodecarboxylation of aqueous PA is facilitated through excitation of its n → π* band, with an absorption maximum of 321 nm (37). This decarboxylation has been known for many years, but the mechanism and resulting products have been controversial (13, 37–39). Earlier studies performed by Leermakers and Vesley (37, 38) report 3-hydroxy-2-butanone (acetoin) as the only isolable product from the aqueous photolysis of PA. The photochemical products were further found to be medium-dependent, with the photochemistry progressing through two different pathways: decarboxylation and reduction. In water, photochemistry of PA progressed through a photodecarboxylation pathway, resulting in significant CO₂ production, as well as acetoin as the major aqueous phase product detected. In organic solvents, such as methanol, chloroform, and ethyl ether, Leermakers and Vesley (37) did not detect CO₂ with photolysis, and thus suggest that the photochemistry is instead progressing through a reduction pathway, with the dimer dimethyltartratic acid found to be the major product in all three of these solvents. Closs and Miller (39) then contend that the production of acetoin in aqueous solution is facilitated by the transition through α-acetolactic acid, a β-keto acid that is known to decarboxylate thermally to acetoin (40). Under similar experimental conditions many years later, Guzman et al. (13) reported no detection of acetoin; instead, they saw two oligomers of PA (dimers) as the major products of this photochemistry, one of which (“Product A”) is the same oligomer (dimethyltartratic acid) detected by Leermakers and Vesley (37) in other organic solvents. In the current work, the photochemistry of PA in aqueous solution is reinvestigated to provide a mechanism for this reaction consistent with the observations reported here and supported by the literature.

Results

Both aqueous and gas phase products were detected using FTIR and UV spectroscopy, NMR, and MS. The photoinduced decarboxylation of aqueous PA was confirmed through IR spectra taken of the gas produced after 2 h of photolysis, as seen in Fig. 1. The intense features between 2,200 and 2,400 cm⁻¹ are due to the CO₂ produced. A closer look at the region between 1,000 and 2,000 cm⁻¹ reveals features due to an additional compound being released into the gas phase concurrent with decarboxylation (Fig. 1, inset), buried beneath the residual water vapor lines. This second gas phase component is identified as acetoin through comparison with the gas phase spectrum of pure acetoin (shown in red in Fig. 1, inset), which was obtained in this laboratory. [Acetoin was initially

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identified by its distinctive odor by one of the authors (B.K.C.). It is important to note that it is difficult to detect acetoin both in the gas phase using FTIR and in an aqueous solution using NMR due to the interference of water.

The NMR spectra (Fig. 2A and B) clearly demonstrate the presence of both acetoin and lactic acid in solution after photolysis. The 1H and 13C NMR of aqueous PA after photolysis yields a complex mixture of products, as shown in Fig. 2F; however, two-dimensional NMR not only provides the chemical shift information of the 1H and 13C NMR, but also the key through-bond correlations present between coupled protons [two-dimensional gradient-selected homonuclear correlation spectroscopy (gCOSY) in Fig. 2A] and between protons and carbons via multiple-bond correlations [gradient-selected heteronuclear multiple bond correlation using matched adiabatic pulses (gHMBC) in Fig. 2B]. These shifts correspond to values from known library data used to identify acetic acid are presented in Fig. S2. The interference of water.

**Fig. 1.** Infrared spectrum of collected gas over 0.1 M aqueous PA after photolysis for 2 h. (Inset) Acetoin features (broad peaks beneath the sharp residual water lines) between 1,000 and 2,000 cm^{−1} (black) with the pure acetoin gas phase spectrum (red) overlaid for comparison. AU, absorbance units.

most of the NMR signals between 1 and 3 ppm is measured to be between 6.5 and 6.9 (×10^{-10} M^{2}/s). The well-resolved signals assigned to acetoin (1H quartet, 4.41 ppm) show D = 10.2×10^{-10} M^{2}/s, lactic acid (1H quartet, 4.36 ppm) gives D = 9.7×10^{-10} M^{2}/s, and acetic acid (1H singlet, 2.07 ppm) gives D = 11.2×10^{-10} M^{2}/s (DOSY data, Fig. 3). For verification of the assignments of acetoin and lactic acid, and to confirm the diffusion measurements, identical DOSY experiments were performed using separate aqueous samples of 0.04 M acetoin and 0.04 M lactic acid. These experiments yielded D = 10.0–10.2×10^{-10} M^{2}/s for acetoin and 9.3–9.6×10^{-10} M^{2}/s for lactic acid, closely matching the values for each compound measured in situ in the photolysis mixture (Fig. S4). Comparing the D values for acetoin and lactic acid with the D values for the majority photolysis products with lower D values, the ratio is found to be in the range of 1.4:1–6:1 (D_{acetoin/lactic acid}/D_{majority product} ratio). Doubling the size/mass of the molecule (i.e., either a homodimer or heterodimer of the small molecules) should lower the measured D value by approximately √2 depending on the molecular geometry, suggesting that the majority of the photolysis products are approximately twofold the size of the individual molecules already identified (i.e., acetoin, lactic acid) (41, 42). These D values indicate that the major products of photolysis of PA are small oligomers. Although no structural information was obtained directly in this work, the size and masses of these oligomers are consistent with the two oligomer products first identified by Guzman et al. (13).

Finally, Fig. 4 presents a UV-visible spectrum of aqueous PA after 1 h of photolysis (black solid line), along with the underlying components of the spectrum shown in broken lines. After 1 h of photolysis, there is still some amount of unphotolyzed PA remaining in the spectrum (scaled experimental spectrum of PA shown as a red broken line in Fig. 4). Acetoin is also seen as an aqueous phase product (scaled experimental spectrum shown as a blue broken line in Fig. 4). The addition of these two components, however, does not account for the entire absorption between 250 and 400 nm shown in Fig. 4. The residual absorption is shown in green (broken line in Fig. 4). This absorption cannot be due to the oligomer dimethyltartaric acid, because it is lacking in a UV chromophore in the wavelength range of interest. Rather, this residual absorption is consistent with another dimer product containing a UV chromophore. A UV-visible absorption spectrum was also taken after 2 h of photolysis and is presented in Fig. S5. After 2 h of photolysis, no new absorbers are apparent in the spectrum, but a further decrease in PA contribution is observed, as well as an increase in the contribution due to acetoin and the oligomer product, consistent with the progression of the same reaction scheme.
Discussion

Aldehydes and, to a lesser degree, ketones are known to hydrate in aqueous solution (43–50). It is known that PA is reversibly hydrated in aqueous solution to its gem-diol and that the equilibrium is both pH- and temperature-dependent, with lower pH and lower temperature both favoring the hydrate (51, 52). In aqueous solution at 298 K, ∼35% of PA exists in its keto form, with the majority existing as its gem-diol (13, 45, 46). The keto form contains a UV chromophore, which can be excited in the near-UV state to induce photolysis. UV irradiation of aqueous PA is known to result in phosphorescence from a3(n,π*) state (53). This triplet is presumed to be involved in the aqueous phase photochemistry of PA. Ab initio calculations (36) have suggested that the S1 state of PA is 1(n,π*) and that this is higher in energy than both the T1 and T2 states, which are found to be 3(n,π*) and 1(π,π*), respectively. Assuming these calculations to be at least qualitatively correct, it seems likely that the UV photochemistry

of PA with light of λ > 300 nm proceeds according to the sequence $S_0 \rightarrow S_1 \rightarrow T_2 \rightarrow T_1$. This intersystem crossing to the triplet surface is markedly different from the gas phase photochemistry, which occurs solely on the singlet surface to generate methylhydroxycarbene (28–30, 54). However, in the aqueous study presented here, PA is seen to react from its $T_1$ state to produce acetoin, lactic and acetic acids, and oligomers, as described below and depicted in Scheme 1.

CBS-QB3 calculations suggest that the $T_1$ state of PA can abstract a hydrogen atom from the carboxyl group of PA with a classical activation enthalpy of 2.7 kcal/mol. The reaction is found to be endothermic by 0.9 kcal/mol at the same level of theory. The corresponding calculation cannot be carried out for hydrogen atom transfer from the carboxyl of the PA hydrate because the resulting carboxyl radical is found to be unbound: It loses CO2 with zero activation barrier. In accord with this finding, the computed transition structure for H-atom abstraction by

![Fig. 2. Superimposed spectra of aqueous 500-MHz NMR spectra of PA after photolysis (red), 0.1 M acetoin (green), and 0.1 M lactic acid (blue). 2D-gCOSY with WET suppression (A) and 2D-gradient gHMBCad (B). The circled peak in B is assigned as acetic acid (further evidence for acetic acid is provided in Fig. S2).](image)

![Fig. 3. DOSY spectrum of photolysis products of PA. Projection of the diffusion dimension (A) and full 2D DOSY plot showing all components (B).](image)
When an intrinsic reaction-coordinate calculation is carried out at the B3LYP/CBSB7 level (which is used for geometry optimization in the CBS-QB3 composite method), it reveals that the reaction is a concerted hydrogen atom transfer and decarboxylation. Hence, the products would be a triplet radical pair with substantial separation between the spins, as shown in reaction 1 of Scheme 1. The overall reaction with the gem-diol has a slightly higher classical barrier (4.3 kcal/mol) than the PA ($T_1$) + PA ($S_0$) reaction (used in ref. 13); however, unlike that reaction, it is exothermic by 22.1 kcal/mol, according to the CBS-QB3 calculations. Thus, although it is conceivable that the photoexcited $T_1$ PA molecule could abstract a hydrogen atom from either a ground-state ($S_0$) PA molecule in its keto or gem-diol form, the reaction with the gem-diol form is used here due to its excess in solution as well as its favorable exothermicity and concerted H-abstraction and decarboxylation.

The radical pair shown in reaction 1 of Scheme 1 will be generated in a solvent cage, but geminate reactions between the radicals will presumably not occur until the pair has undergone intersystem crossing to a singlet-coupled state. In competition with this, escape of the radicals from the cage is likely. Hence, one must consider several possible radical–radical reactions. Two of these reactions, resulting in products detected in this work, are shown in reactions 2 and 3 of Scheme 1. The product of reaction 2 is a hydrate of acetolactic acid. Its dehydration should be thermodynamically favorable because, unlike PA hydrate, the product is not an α-keto acid. Decarboxylation of acetolactic acid, known to occur within minutes at 25 °C in aqueous solution (39, 40), would yield acetoin, a principal product of aqueous PA photolysis. This sequence is depicted in reactions 4a–4c of Scheme 1. Finally, reaction 3 of Scheme 1 is a disproportionation that generates lactic and acetic acids, both of which are observed products of aqueous PA photolysis here (NMR results, Fig. 2). The alternative disproportionation (SI Additional Radical–Radical Reactions) would generate ground-state PA and the hydrate of acetaldehyde, which is also a known product of PA photochemistry (37) but was not detected here. In addition, there could be other recombination and disproportionation reactions occurring (SI Additional Radical–Radical Reactions). These may be kinetically important, but they are not significant in terms of product identification because they generate products already considered in Scheme 1 or products that are not observed here, and hence they are not depicted explicitly.

In addition to acetoin and lactic and acetic acids, small oligomers (dimers) were observed in this work, in the previous work by Guzman et al. (13) in aqueous solution, and by Leermakers and Vesley (37) in organic solvents. Reaction 5 of Scheme 1 shows the generation of 2,3-dimethyltartaric acid, presumably in both meso- and DL diastereomers, from the reaction between two molecules of the prevalent radical intermediate (PA$^\bullet$). This same oligomer has been identified in earlier studies (13, 37), and it is detected in the present work as a significant product of aqueous PA photochemistry using MS (Fig. S3). This dimer product is also consistent with the approximate size of oligomers detected using DOSY NMR (Fig. 3). Although at least one other dimer product is detected in this work, as described in Results,

![Scheme 1. Summary of the proposed mechanism for aqueous PA photochemistry.](image-url)
because no structural information is available, it is not included in the mechanism presented here.

One key feature of our mechanism is the concerted hydrogen atom transfer and decarboxylation shown in reaction 1 of Scheme 1. According to our CBS-QB3 calculations, the radical H₂C−C(OH)−CO₂• results from H-abstraction from the gem-diol of PA is unbound; it decarboxylates with zero barrier. This results in the concerted H-abstraction and decarboxylation proposed here. By contrast, the radical H₂C−CO−CO₂•, resulting from H-abstraction from a PA molecule in its keto form, is found to be bound at the same level of theory. This emphasizes the need for water in the solution phase photodecarboxylation chemistry presented here (reactions 1–4 in Scheme 1). The concerted H-atom transfer and decarboxylation of reaction 1 of Scheme 1 require the presence of the gem-diol, which is formed only in aqueous environments.

There are a few key points to emphasize concerning this aqueous phase mechanism. First, it is important to note that CO₂ is produced in aqueous solution concurrent with the formation of acetoin and lactic and acetic acids but is not required in the production of the oligomer dimethyltartaric acid. In our mechanism, the formation of dimethyltartaric acid (reaction 5 of Scheme 1) does not require water or necessarily the production of CO₂, merely a good H-atom donor to produce the radical intermediate PAs. Leermakers and Vesley (37) originally proposed this to explain their observation of photo-reduction in organic solvents (in contrast to photodecarboxylation), proposing H-abstraction facilitated by reaction of the T₁ state of PA with a solvent molecule, resulting in PAs formation followed by a self-reaction to form dimethyltartaric acid. Our results are consistent with this assertion. It is also interesting to note that gas phase photolysis does not require the presence of water for decarboxylation (37), whereas solution phase decarboxylation chemistry does. This is likely due to the fact that gas phase photochemistry of PA occurs predominantly on the singlet surface, with PA directly decarboxylating in a unimolecular reaction to form a methylene hydrocarbene. This is followed by H-atom transfer to form acetaldehyde and vinyl alcohol (28, 54). In water, however, the chemistry occurs on the triplet surface, proceeding bimolecularly through reaction of one molecule of PA in the T₁ state with one molecule of PA in its gem-diol form. Water appears to be playing a role in energy transfer and decarboxylation shown in reaction 1 of Scheme 1.

This photochemistry of PA in aqueous solution is also known to be pH-sensitive, with the protonated form of PA decarboxylating with a yield nearly 20-fold that of the anionic form (pyruvate) at higher pH values (37), an observation that is consistent with the mechanism presented here. The presence of the acid hydrogen atom is essential to the decarboxylation chemistry, confirming the first abstraction: the decarboxylation reaction of Scheme 1. It is interesting to note that this pH effect is exactly the opposite of what has been found to occur for reaction with OH (16), a competing removal pathway for PA in the troposphere. This indicates that in aqueous environments, the dominance of either direct photolysis or OH reaction in the removal of PA may itself be pH-dependent.

Finally, it has been observed previously that UV irradiation (λ > 300 nm) of aqueous PA glass at 77 K results in the formation of triplet-coupled radical pairs with a separation of ≥5 Å between the spins, which is accompanied by ultrafast decarboxylation (55). The explanation for this last observation is long-range electron transfer between the S₂ and T₁ states of PA, resulting in a triplet-coupled radical ion pair. The radical cation component of this pair is proposed to be responsible for the decarboxylation (13, 55). The mechanism presented in this work provides an alternative explanation for this cryogenic aqueous glass photochemistry. During the concerted H-abstraction and decarboxylation of reaction 1 in Scheme 1 (transition state structure depicted in Fig. S7), the carbons that carry the highest spin density in the products are already separated by 5.5 Å in the transition structure. It seems that this mechanism could provide an alternative explanation of the EPR spectrum, resulting in similar spin separations, and the ultrafast decarboxylation seen in the aqueous glass photochemistry of PA, in lieu of the radical ion pairs previously proposed (55).

**Atmospheric Implications**

The contrast between the chemistry performed by UV photolysis of gaseous and aqueous phase PA highlights the importance of a thorough understanding of chemistry as a function of the molecule’s environment for inclusion in atmospheric models. This work shows that photochemical processes in the aqueous phase of aerosols result in different products than in the analogous gas phase chemistry, thus affecting aerosol composition and optical properties differently. The bulk ocean is slightly basic, causing the progression of this reaction scheme near the ocean surface (where UV light still penetrates) to be unlikely due to the presence of PA predominantly in its anionic form. Atmospheric aerosols, however, are known to experience a wide range of pH values throughout their atmospheric lifetime, and can reach acidic pH values at which this chemistry will become dominant (56). These aerosol particles have the added advantage of concentrating the reactant species through selective evaporation of water, resulting in high concentrations of reactant monomers (57–61). Therefore, although this chemistry is unlikely to be an important contributor to bulk ocean chemistry, it will be important in acidic aqueous atmospheric aerosols. In addition, the production of acetoin, which partitions both to the aqueous phase and the gas phase, may contribute to the seeding of new particles. Finally, the direct photolysis of aqueous PA presented here, as well as the known competing OH reaction pathway, results in the formation of oligomers, a unique product to the aqueous phase chemistry (compared with the gas phase chemistry), which have been implicated in SOA formation (1, 5, 12, 14).

**Materials and Methods**

PA (98%) was purchased from Sigma–Aldrich and was distilled under reduced pressure before its preparation to a final concentration of 0.1 M in distilled water, a typical concentration for atmospheric aerosol particles (5, 6). Acetoin (≥92%, natural) was also purchased from Sigma–Aldrich, and it was prepared to a final concentration of 0.04 M in distilled water without further purification. Similarly, lactic acid (racemic, meets US Pharmacopeia testing specifications, purchased from Sigma–Aldrich) was prepared to a final concentration of 0.04 M in distilled water without further purification.

Aqueous PA was photolyzed using a 450-W Xe arc lamp (Newport) for 1–2 h, while kept chilled at 4 °C in a temperature-controlled water bath. A Xe lamp was used due to the similarity of its output to the solar spectrum. The photolyzed PA solution was allowed to return to room temperature before any subsequent analysis was performed.

**UV-Visible Spectroscopy.** UV-visible spectra were obtained of aqueous samples using a USB2000 miniature fiber optic UV-visible spectrometer from Ocean Optics.

**IR Spectroscopy.** The gas that evolved during photolysis of aqueous PA was collected over the solution during 2 h of photolysis. Then, after the solution was allowed to return to room temperature, a gas phase IR spectrum was obtained of the evolved gaseous products using the internal compartment of a Bruker Tensor 27 FTIR spectrometer, purged with dry house air. Spectra were collected at a resolution of 1 cm⁻¹ and were averaged over 50 scans.

**NMR.** NMR spectra were acquired using a Varian INOVA 500-MHz NMR spectrometer operating at 499.60 MHz for ¹H observation. All samples were prepared with a volume of 0.8 mL in 5-mm NMR tubes. A total of 0.050 mL of water (99.9% (mole %) deuteration of the deuterated solvent) D₂O was added to provide a field-frequency lock, making the final solvent 95% (vol/vol) H₂O and 5% (vol/vol) D₂O. To characterize the key components of the photolysis products fully, a combination of standard high-resolution NMR experiments, such as 1D ¹H NMR, 2D gCOSY, gHMBCad, gHSQCad, and high-resolution...
Computation. Electronic structure calculations used the CBS-QB3 composite method (62), as implemented in the Gaussian 03 suite of programs (63). Cartesian coordinates and energies of stationary points are included in Dataset S1.

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**Supporting Information**

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**SI Additional Radical–Radical Reactions**

An alternative disproportionation reaction to reaction 3 of Scheme 1 is shown below in reaction \(i\). This would generate ground state pyruvic acid (PA) and the hydrate of acetaldehyde, which is also a known product of PA photochemistry but was not detected here.

![Reaction i](image)

Another possible symmetrical recombination reaction (in addition to reaction 5 as shown in Scheme 1) is shown below in reaction \(ii\).

![Reaction ii](image)

Reaction \(ii\) would generate a double hydrate of butane-2,3-dione, which has not been reported or detected here as a product of PA photochemistry, and would probably not be stable under the photochemical reaction conditions (1). In addition to the symmetrical recombination reactions shown in reaction 5 of Scheme 1 and reaction \(ii\) shown above, there could presumably be disproportionation reactions involving hydrogen atom transfers between the radicals. As stated in the main text, these are not shown explicitly because they will generate products already considered in the reactions shown in Scheme 1.

**SI Materials and Methods**

To perform NMR with 1H detection in aqueous solution, WET solvent suppression was used to eliminate >99% of the \(H_2O\) signal (2). To suppress the NMR signal from water adequately while not attenuating peaks near water, a very narrow band-selective pulse of 1,080 \(\mu s\) was used, allowing nearly quantitative detection of \(^1\)H signals that are observed less than 0.4 ppm from the solvent resonance. Diffusion ordered spectroscopy experiments were performed with compensation of nonuniform gradients, convection compensation using the software tools provided in the VNMRJ V 3.2A software (Agilent Technologies, Inc.), and calibration using the residual signal of pure \(D_2O\) at a calibrated temperature of 25 °C (3). In all cases, \(^1\)H detection experiments were performed using the optimized WET water suppression mentioned above as the initial preparation step of the NMR pulse sequence. The two-dimensional gradient-selected heteronuclear single-bond correlation spectrum using matched adiabatic pulses (2D-gHSQCad) experiments were performed with matched adiabatic sweeps for coherence transfer, corresponding to a central \(^13\)C-\(^1\)H coupling constant of 146 Hz (4). Gradient-selected heteronuclear multiple bond correlation using adiabatic pulses (gHMBCad) experiments were optimized for a long-range \(^13\)C-\(^1\)H coupling constant of 8.0 Hz.

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Fig. S1. 2D WET gHSQCad of aqueous PA sample after photolysis. Cross-peaks corresponding to acetoin are labeled accordingly.
Identification of acetic acid in photolysis product: gradient-selected heteronuclear single-bond correlation using matched adiabatic pulses (gHSQCad) and gHMBCad NMR of PA after photolysis, showing the indirect detection of $^{13}$C signals at 20.6 and 176.8 ppm, respectively, via through-bond correlation to the singlet at 2.07 ppm. All three of these mutually correlated NMR shifts agree with published library values for acetic acid obtained from the spectral libraries of ADC Labs’s NMR Predictor software.

Negative ion electrospray ionization TOF mass spectrum after 2 h of photolysis. Major peaks displayed are unphotolyzed PA (87.02 m/z) and two oligomer products (175.07 m/z and 177.05 m/z).
Fig. S4. Convection-compensated diffusion ordered spectroscopy (DOSY) spectra of 0.1 M aqueous acetoin (A) and 0.1 M aqueous lactic acid (B). DOSY parameters: $\delta = 2.0$ ms, $\Delta = 60.0$ ms, $G = 28$ gradient values ranging from 14.9–49.8 G/cm.
Fig. S5. UV-visible absorption spectrum of aqueous PA after 2 h of photolysis (black) with underlying components shown in broken lines: PA (red), acetoin (blue), and residual oligomer absorption (green). AU, absorbance units.

Fig. S6. 2D WET gradient correlation spectroscopy [two-dimensional gradient-selected homonuclear correlation spectroscopy (gCOSY)] spectrum of aqueous PA sample after photolysis.
Fig. S7. B3LYP/CBSB7 transition structure for the reaction of the PA $T_1$ state with the ground state PA hydrate. An intrinsic reaction coordinate calculation reveals that this is the transition state for a concerted H-atom transfer and decarboxylation.

Fig. S8. 2D WET adiabatic gradient heteronuclear multiple-bond correlation (gHMBCad) of aqueous PA sample after photolysis.

Other Supporting Information Files

Dataset S1