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Comment

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Reply to "Comment on 'Reactivity of Ketyl and Acetyl Radicals from Direct Solar Actinic Photolysis of Aqueous Pyruvic Acid'"

Alexis J. Eugene and Marcelo I. Guzman*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, United States

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Supporting Information

BACKGROUND ON PYRUVIC ACID PHOTOCHEMISTRY IN WATER AND ICE

The photochemical study of pyruvic acid (PA) in water by Eugene and Guzman (E&G)[1] considered the integration of a body of work in water and ice[2−9] that Vaida and co-workers (V&C)[10] have partially ignored and misrepresented. The reaction mechanism in these PA photochemistry studies in water and ice[4] not only identified the photoproducts but also integrated knowledge gained by (1) studying the reaction intermediates generated concomitantly to photodecarboxylation at cryogenic temperature,[3] (2) measuring the kinetics of the reaction both in the condensed phase and the evolution of gases at variable temperature,[2,3,5,7] (3) exploring the dynamic nature of the hydration equilibrium at variable temperature in water and ice,[6] (4) determining the dependence of the quantum yield on the initial $[PA]_0$,[1,5] (5) investigating the effect of variable concentration of radical scavengers such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and dissolved O_2,[1,5,7] (6) measuring solvent kinetic isotopic effect (KIE)[1] as well as using isotopic labels,[1,3,5] and (7) contrasting the optical absorptivity and molecular composition of the mixtures of identifiable aliphatic polyfunctional oligomers obtained during photobleaching and thermochromism cycles.[8,9]

For atmospheric relevance the "*experiments*" with PA reported in all figures by E&G were in air (cf. the corresponding experimental section), and any photolyses under 1 atm $N_2(g)$ or $O_2(g)$ were referred to as "*controls*".[1] The results from E&G[1] strongly supported a sound reaction mechanism[2−8] that had included the generation of thermolabile 2-(3-oxobutan-2-yloxy)-2-hydroxypropanoic acid (oxo-C_7 product) and 2-(1-carboxy-1-hydroxyethoxy)-2-methyl-3-oxobutanoic acid (oxo-C_8 product) with hemiketal structures.[1,5,7] Despite the fragility of these products, they are stable enough at room temperature to be first separated by ultrahigh pressure liquid chromatography (UHPLC) and ion chromatography (IC) and then fragmented by collision-induced dissociation during mass spectrometry (MS).[1,4] Additional support for the existence of these products arose from isolating their anions with an Orbitrap high-resolution mass spectrometer (HRMS), which enabled studying their fragmentation.[1] Instead, when analyzing the photoproducts at elevated-temperature gas chromatography (GC), these hemiketals thermally decompose into acetoin, which should not be mistaken as a photoproduct.[1,2,4,5,7]

PHOTOCHEMICAL INITIATION AND CAGE RECOMBINATION

In opposition to the need from V&C to create a divergent mechanism,[10] E&G have clearly indicated that "*For practical purposes, there is no difference if the (indistinguishable) photoinduced bimolecular process represents a hydrogen atom transfer, an electron transfer, or proton-coupled electron transfer (PCET)*".[1] In other words, the same reactive species, ketyl (K·) and acetyl (Y·) radicals, are generated in all cases after the photogeneration of a triplet excited state of PA.[1] The primary decarboxylation reaction that generates Y· from an acyloxy radical (Scheme 1 of E&G)[1] propels the process in an irreversible direction.[3] The only way to form new C−C or C−O bonds to achieve products of higher molecular weight is by recombination of the prevalent photogenerated radicals from different solvent cages (otherwise the original molecules would be regenerated).[3]

Different recombination reactions among the produced radicals have been considered by Guzman et al. and E&G,[1,3,5,7] including the recombination of Y· (and its hydrate) and K·. However, the reaction Y· + K· was experimentally discarded, because α-acetolactic acid standard (1) was confirmed to be absent in the mixture of photoproducts and (2) remained stable while important evolution of CO_2 occurred during the postphotolysis period in the dark below 4 °C.[1,5,7] E&G have acknowledged the key radicals (K· and Y·) participate in the same mechanism in water and ice,[1] which proceeds to form 2,3-dimethyltartaric acid (DMTA) and 2-hydroxy-2-((3-oxobutan-2-yl)oxy)propanoic acid (oxo-C_7 product).[3−5] The unique oxo-C_7 product results from a β-ketocarboxylic acid decarboxylation of the very unstable primary photoproduct, 2-(1-carboxy-1-hydroxyethoxy)-2-methyl-3-oxobutanoic acid (oxo-C_8 product) with a rate constant $k = 1.21 \times 10^{-3}$ s^{-1} at 25 °C.[3,5,7] The generation of the oxo-C_8 product (all structures are displayed in Scheme S1, Supporting Information) involves the participation of a very reactive K·, which attacks the carbonyl of PA forming a radical C· that combines with Y· as shown in Scheme 1 of E&G,[1,3,5,7] an important reaction overlooked by V&C. Despite the claim by V&C,[10] E&G never invoked the participation of a tertiary alcohol.[1] The transition state of the oxo-C_8 product favors the

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fast β-ketocarboxylic acid decarboxylation[7] that forms an oxo-C_7 product prestabilized by intramolecular H-bonds.[11,12]

QUANTITATIVE KINETIC AGREEMENT BY MULTIPLE ANALYTICAL METHODS

E&G have advanced previous efforts by quantifying the generation of 2,3-dimethyltartaric acid, acetic acid, and the oxo-C_7 and oxo-C_8 products by combining the use of separations by UHPLC and IC coupled to MS, HRMS, the assignment of one-dimensional (1D) ^{1}H and ^{13}C NMR and two-dimensional (2D) ^{13}C gCOSY spectroscopic features, as well as by employing quantitative ^{1}H NMR (qNMR).[1] The chromatographic separations were performed both with reversed-phase C18 and alkanol quaternary ammonium columns with high specificity to separate monocarboxylic, dicarboxylic, and oxocarboxylic acids prior to UV−visible, conductivity, and MS detection.[13,14] In addition, these analyses included the separation, identification, and quantification of carbonyls (C═O) in the mixture of photoproducts treated with 2,4-dinitrophenylhydrazine (DNPH).[1,2,15] The undeniable power of these techniques for the analysis of this class of products,[1,2] with low limits of detection (LOD) also makes them excellent for the determination of lactic acid (LOD = 86 nM) and acetoin (LOD = 330 nM)[1] after chromatographic separation, as exemplified by applications for food industry and clinical settings.[16−19] The work of E&G used standard addition of lactic acid and acetoin directly into the samples, providing an unambiguous comparison of the spectroscopic features and facilitating the quantification process.[1] Furthermore, the multiple analytical techniques employed and listed above, not only HRMS as stated by V&C,[10] provided confirmation that a major oxo-C_7 product is observed both in experiments under 1 atm air or in controls under 1 atm N_2(g).[1]

DISCUSSION AND INTERPRETATION OF NEW RESULTS

E&G have also carefully attempted to detect lactic acid and acetoin by ^{13}C and ^{1}H NMR, HRMS in the condensed phase, and Fourier transform infrared (FTIR) spectroscopy for the hypothetical transfer of volatile acetoin to the gas phase, concluding that neither of these species are photoproducts of PA.[1,2] Moreover, the work of E&G has routinely employed IC to ensure reagent purity.[1] For example, Figure 1A shows that, during dark storage (more than three months) of distilled pyruvic acid in the refrigerator, the production of four impurities (lactic, acetic, parapyruvic, and zymonic acids) proceeds, requiring repeated purification.[1] Lactic, parapyruvic, and zymonic acids have not been observed as photoproducts when working with freshly distilled PA.[1] However, V&C state that lactic acid and acetoin are minor photoproducts in the absence of dissolved O_2 based on a series of 2D NMR measurements[10,20,21] and assert that *"... if sufficient oxygen is present during photolysis, the formation of acetoin and lactic acid is severely inhibited,"*[10] implying that more acetoin and lactic acid would be observed in the absence of O_2(aq). Therefore, Figure 1B,C shows the ^{1}H NMR spectrum for a photolysis control performed under 1 atm N_2(g) for the region corresponding to the $-CH_3$ doublets of lactic acid (~1.42 ppm in Figure 1B) and acetoin (~1.36 ppm in Figure 1C). Figure 1B,C, respectively, agrees with those for the experiment in air displayed in Figures 6D and S7 of E&G.[1] Indeed, the spike additions of lactic acid (red line in Figure 1B) and acetoin (pink line in Figure 1C) to

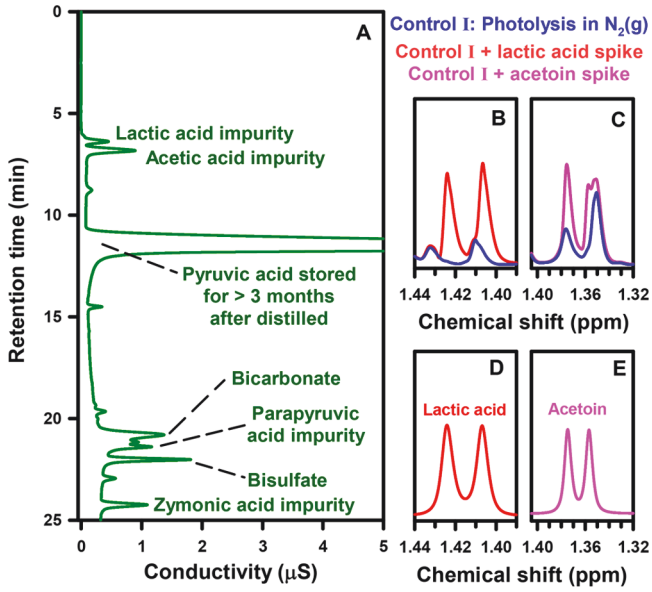

Figure 1. (A) Ion chromatogram for PA (m/z 87) stored in the refrigerator for more than three months after it had been distilled showing its alteration by the development of impurities: lactic (m/z 89), acetic (m/z 59), parapyruvic (m/z 175), and zymonic (m/z 157) acids. Bicarbonate (m/z 61) and bisulfate (m/z 97) are also labeled. All anions were assigned with available standards and/or using the m/z values (given in parentheses) obtained by mass spectrometry. These results supplement those from ref 1 identifying acetic, parapyruvic acid and zymonic acid impurities and show that only freshly distilled PA can be used as a reagent for photochemistry studies. (B) ^{1}H NMR spectrum for (blue) the $-CH_3$ group doublet centered at ~1.42 ppm in a control with 100.1 mM PA at pH 1.0 photolyzed at $\lambda \geq 305$ nm for a 50% reagent conversion under continuous sparging with N_2(g), and (red) the mismatch for this doublet after spiking to $[\text{D,L-lactic acid}]_{\text{final}}$ = 9.34 mM. (C) ^{1}H NMR spectrum for (blue) the $-CH_3$ group doublet centered at ~1.36 ppm in the same control in panel B, and (red) the mismatch for this doublet after spiking to $[\text{acetoin}]_{\text{final}}$ = 10.02 mM. The corresponding spectral regions for (D) D,L-lactic acid and (E) acetoin standards are shown for comparison of the position, line shape, and intensity ratio for the peaks in these $-CH_3$ doublets. ^{1}H NMR spectra were recorded on a 400 MHz Varian Inova spectrometer using a WET 1D water-suppression pulse sequence. Samples were prepared to contain 10% v/v D_2O with 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) reference and gadolinium(III) chloride hexahydrate as described in ref 1.

the photoproducts (blue line in Figure 1B,C) show the mismatch in the chemical shift position, line shape (appearance of new peaks or shoulders), and intensity ratio for the $-CH_3$ doublets after spiking to $[\text{D,L-lactic acid}]_{\text{final}}$ = 9.34 mM and $[\text{acetoin}]_{\text{final}}$ = 10.02 mM, respectively. For comparison, the corresponding spectral regions for D,L-lactic acid and acetoin standards are shown in Figure 1D,E, respectively. The indistinguishable chemical shifts for (1) the singlet $-CH_3$ peaks at ~2.21 ppm and (2) the weak quartet −CH peaks at ~4.40 ppm in both the oxo-C_8 product and acetoin justified choosing the doublet centered at ~1.36 ppm for the comparison provided in Figures 1C.[1] Thus, rather than assigning the peaks in question to lactic acid or acetoin, these $-CH_3$ resonances and those at ~2.31 and ~2.21 ppm (Figure 6 and Table S3 of E&G)[1] should be assigned to the oxo-C_7 and oxo-C_8 products, and not to any other species. Figure S1 (Supporting Information) provides IC analyses supporting the above interpretation of Figure 1B.

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The multiple methods and conditions used to study the photochemistry of PA by E&G ruled out the production of lactic acid and acetoin.[1] Therefore, we attribute cross peaks A, B, D, E, F, and G in the 2D NMR spectrum (Figure 4 of E&G)[1] to a species other than lactic acid or acetoin, namely, our oxo-C_7 product. The total acquisition time of this 2D spectrum had limited the f1 line widths and peak heights of Figure 4 in E&G.[1] Thus, a new $^{13}C-^{13}C$ gCOSY spectrum from a photolysis experiment performed under continuous air sparging of aqueous PA is displayed in Figure 2. The presence

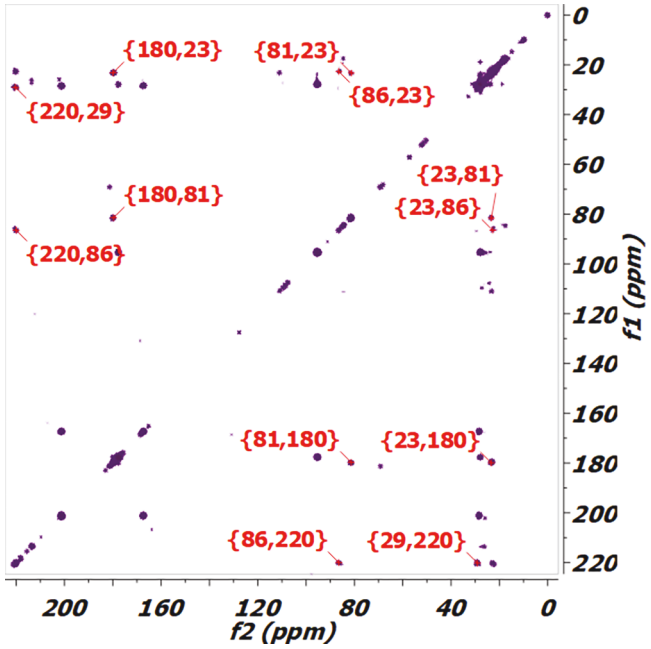

Figure 2. $^{13}C-^{13}C$ gCOSY NMR spectrum for an experiment with 111.3 mM ^{13}C PA in D_2O at pD = 1.0 photolyzed at $\lambda \geq 305$ nm for a 50% reagent conversion under continuous sparging with air. Spectra were recorded during 72 h at 298 K on a Varian VNMRS-700 spectrometer equipped with a 5 mm $^1H\{^{13}C,^{15}N\}$ carbon-enhanced cold probe at 18 K using a standard gCOSY sequence with 90° pulses and a t_1 delay of 20 ms. The f2 dimension was acquired with 2048 points, while the f1 dimension recorded 512 increments. A total of 96 scans were recorded per FID of a sample prepared with DSS reference and gadolinium(III) chloride hexahydrate as described in ref 1.

of cross peaks previously labeled B (86 ppm, 220 ppm), D (86 ppm, 29 ppm), and E (81 ppm, 23 ppm) on both sides of the diagonal of Figure 2 verify that they correspond to true couplings putting to rest V&C's concerns[10] about them.

While V&C indicated cross peak C appeared on the diagonal[10] of Figure 4 from E&G, the label had been pointed to a very weak spot located slightly off the diagonal at ~81 and ~86 ppm, as expected from a two-bond coupling.[1] However, the weak (~2−3 Hz) coupling for the C−O−C(OH) cross peak[22] would require a long delay t_1 between pulses to fully manifest, and it is expected to be much weaker than the others, since a maximum of 20 ms was used for Figure 2. Using a long delay t_1 = 150 ms[23] for the gCOSY experiment was impractical, because all the signals of interest in the oxo-C_7 product vanished. The absence of previously labeled cross peak C at the intersection of ~81 and ~86 ppm in Figure 2 is readily explained by the *J*-coupling constant and should not be used to interpret that the cross peaks A, B, D and E, F, and G belong to two different molecules. Instead, the absence of this coupling only indicates that both sets of peaks belong to different spin systems, which may exist in the same molecule, separated by a heteroatom as for the corresponding oxo-C_7 product.[1] This is the reason for E&G to have used multiple analytical methods and measured the abundance of different products over time by qNMR.[1] Moreover, the integrals for the three $-CH_3$ resonances at 29.3, 23.2, and 22.8 ppm in the 1D ^{13}C NMR spectrum are equivalent, confirming that the cross peaks from both spin systems analyzed in Figure 2 belong to a unique molecule. Thus, the ^1H NMR peaks assigned to acetoin by V&C in Reed Harris et al.[24] must have actually corresponded to another product.[1] Curiously, this alternative product with a molecular weight of 176 amu (anion with m/z^- 175) was previously ignored[20,24,25] but recently proposed by V&C to be 2,4-dihydroxy-2-methyl-5-oxohexanoic acid (DMOHA) without experimental confirmation,[26] which is a simple C−C bridge isomer of the oxo-C_7 product proposed by E&G.[1,5,7] Assigning the structure of DMOHA to the species with formula $C_7H_{12}O_5$ is problematic due to its stability at high-temperature GC conditions. Instead, the molecule of $C_7H_{12}O_5$ is fragile and known to decompose into acetoin in agreement with the structure for the oxo-C_7 product.[5] Moreover, the formation mechanism of DMOHA from V&C utilizes the same *β*-ketocarboxylic acid decarboxylation proposed by E&G,[1] except that the oxo-C_8 precursor is generated from H atom abstraction from parapyruvic acid impurity,[26] which should not participate in the formation of such an abundant PA photoproduct. E&G had verified parapyruvic acid is absent before and after the photoreaction when starting with freshly distilled PA.[1] The $-CH_2-$ group participating in the C−C bridge in DMOHA proposed by V&C in Rapf et al.[26] can be reasonably predicted to appear at ~44 ppm in the ^{13}C NMR spectrum in water.[27] However, neither a resonance in the ^{13}C NMR spectrum in Figure S5 from E&G[1] at 44 (±10) ppm nor a cross-peak involving such a $-CH_2-$ in Figure 2 is observed, justifying the need for an alternative C−O−C bridge in the structure of the oxo-C_7 product. Finally, in agreement with previous findings,[5] the large kinetic isotope effect KIE_{-PA} = 9.09 measured in H_2O relative to D_2O for the initial loss of PA discarded the possibility of a nonlinear transition state[1] as would have occurred for H atom abstraction from the $-CH_3$ group of PA implied by V&C in their mechanism.[20,24,26]

Fundamental mechanistic questions about the complex photochemical processing of aqueous PA have been reexamined herein resulting in a comprehensive rebuttal to V&C's[10] untested reinterpretation of our datasets. In conclusion, the new physical insights presented here strongly support the structures and mechanism proposed by E&G,[1] which arose from a combination of analytical techniques and previous work.[1−3,5−9,28−32]

■ ASSOCIATED CONTENT

Supporting Information

Figure S1 and Scheme S1. This material is available free of charge via the Internet at http://pubs.acs.org/. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b08273.

Ion chromatography for a photolysis control in $N_2(g)$, chemical structures discussed in main text (PDF)

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AUTHOR INFORMATION

Corresponding Author

*E-mail: marcelo.guzman@uky.edu. Phone: (859)323-2892.

ORCID

Marcelo I. Guzman: 0000-0002-6730-7766

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

DMOHA, 2,4-dihydroxy-2-methyl-5-oxohexanoic acid; DNPH, 2,4-dinitrophenylhydrazine; DSS, 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt; E&G, Eugene and Guzman; GC, gas chromatography; gCOSY, gradient correlation spectroscopy; HRMS, high-resolution mass spectrometry; IC, ion chromatography; K·, ketyl radical; LOD, limit of detection; MS, mass spectrometry; NMR, nuclear magnetic resonance; oxo-C_8 product, 2-(1-carboxy-1-hydroxyethoxy)-2-methyl-3-oxobutanoic acid; oxo-C_7 product, 2-(3-oxobutan-2-yloxy)-2-hydroxypropanoic acid; PA, pyruvic acid; qNMR, quantitative ^{1}H NMR; UHPLC, ultrahigh pressure liquid chromatography; V&C, Vaida and co-workers; Y·, acetyl radical; 1D, one-dimensional; 2D, two-dimensional

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