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Photoinduced oligomerization of aqueous pyruvic acid

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The 320 nm-band photodecarboxylation of aqueous pyruvic acid, PA, a representative of the α-oxocarboxylic acids widely found in atmospheric aerosol, yields 2,3-dimethyl tartaric, A, and 2-(3-oxobutan-2-yloxy)-2-hydroxypropanoic, B, acids, rather than 3-hydroxy-2-oxobutanone as previously reported. A and B are identified by liquid chromatography with UV and ESI MS detection, complemented by collisional induced dissociation and ^{2}H- and ^{13}C-isotope labeling experiments. The multifunctional ether B gives rise to characteristic $\delta \sim$80 ppm ^{13}C-NMR resonances. CO_2(g) release rates during PA photolysis are halved, while A and B are suppressed by the addition of $>$1.5 mM TEMPO. A and B are partially quenched in air-saturated solutions. The quantum yields of A and B formation increase with PA concentration as [PA](a + [PA])$^{-1}$ in the range $5 \leq$ [PA]/mM ≤ 100. These observations are consistent with a free radical oligomerization process initiated by a bimolecular reaction between ^{3}PA* and PA leading to ketyl, $CH_3C(OH)C(O)OH$, and acetyl, $CH_3C(O)\cdot$, carriers, rather than by $^{3}PA^{*}$ unimolecular decomposition into 1-hydroxyethylidene, $^{3}CH_3C(OH)$**:** (+ CO_2), or [$CH_3C(O)\cdot$ + $\cdot C(O)OH$]. A arises from the recombination of ketyl radicals, while B ensues the decarboxylation of a C_8 β-ketoacid formed by association of acetyl radicals with the ketyl radical adduct of PA. Since the radical precursors to A and B are inefficiently scavenged by O_2 ($k_{sc} \sim 1 \times 10^{6} M^{-1}$ s^{-1}) in this system, PA is able to oligomerize into multifunctional polar species in aerated aqueous solutions under solar illumination.