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Characterization of Polyfunctional Oligomers From Pyruvic Acid Photolysis in Water

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Humic substances (HUMICS) are widespread in natural surface waters, where they ultimately undergo solar photolysis into small alpha-dicarbonylic species, such as glyoxal, glyoxylic and pyruvic acids. Humic-like substances (HULIS) are also found in the atmospheric aerosol. We report a laboratory study of the photolysis of aqueous pyruvic acid (PA), solutions at concentrations representative of the atmospheric aerosol using UV-absorption, high resolution electrospray mass (EMS), and nuclear magnetic resonance (NMR) spectrometries. PA yields polyfunctional oligomers reaching molecular masses of up to 900 Da, some of which absorb into the visible. Exact mass determinations (to the fourth decimal place) yielded unique molecular formulae in most cases, which were confirmed by collisionally induced dissociation (CID) patterns and the analysis of the products of photolysis of [2-^{13}C] and [3-^{13}C] PA isotopologues. The lowest energy CID channels corresponded to neutral fragment losses of masses: 18 (H_2O), 44 (CO_2), 46 (HCOOH) and 62 (CO_3H_2. ^{13}C- and ^{1}H- NMR of [2-^{13}C] and [3-^{13}C] PA photolysis mixtures revealed the presence of various carbonyl functionalities (190 to 230 ppm) displaying ^{2}J(CC) and ^{3}J(CC) couplings among themselves and with anomeric carbons ($\sim$ 96 ppm). Based on this evidence, we propose molecular structures and a mechanism of formation for these oligomers..