Kinetics and Mechanisms of Aqueous-Phase Photosensitized Reactions of Imidazole-2-carboxaldehyde and 3,4-Dimethoxybenzaldehyde with α,β-Unsaturated Carbonyl Compounds

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Light-absorbing compounds in the atmospheric aqueous particulate phase, i.e., photosensitizers, can initiate photochemical reactions to form secondary organic aerosol (SOA). Although several studies have been conducted on the formation and aging of SOA, the influence of photosensitizers in the aqueous and particulate phases is still far from completely understood since kinetic data, product analyses, and mechanisms of the photosensitized reactions are still rare. Within the present study, we focus on the photosensitized reactions of methyl vinyl ketone (MVK), methacrolein (MACR), and methacrylic acid (MCA) in the aqueous phase by excited 2-IC (imidazole-2-carboxaldehyde). The reactions were investigated in terms of kinetics and their product formation. To this end, laser flash excitation-laser long-path absorption and ultra-performance liquid chromatography coupled with high-resolution electrospray ionization spectrometry were used. The second-order reaction constants of excited imidazole-2-carboxaldehyde (2-IC) with MVK: $k = (1.0 \pm 0.1) \times 10^9$ L mol^{-1} s^{-1} at pH 4 − 5 and 9, with MACR: $k = (1.4 \pm 0.4) \times 10^9$ and $k = (1.5 \pm 0.1) \times 10^9$ L mol^{-1} s^{-1} at pH 4 − 5 and 9, and with MCA: $k = (1.4 \pm 0.4) \times 10^9$ and $(1.1 \pm 0.4) \times 10^8$ L mol^{-1} s^{-1} at pH 4 − 5 and 9 were determined. In the product studies, the main products of the reaction between 2-IC and MVK, in the monomer form as well as the dimer form, were observed. In a similar manner, the addition reactions between 3,4-dimethoxybenzaldehyde (DMB) and MVK were investigated. In case of the excited DMB the second-order reaction constants with MVK: $k = (1.5 \pm 0.1) \times 10^9$ L mol^{-1} s^{-1} at pH 9, with MACR: $k = (1.1 \pm 0.1) \times 10^9$ and $k = (2.8 \pm 0.5) \times 10^9$ L mol^{-1} s^{-1} at pH 2 and 9, and with MCA: $k = (1.4 \pm 0.4) \times 10^9$ at pH 9 were obtained. The product studies revealed that an addition reaction of excited 2-IC or excited DMB with the double bond compounds used produced high molecular weight compounds. The data received will be used to propose a reaction mechanism that will be incorporated into the CAPRAM model to evaluate the influence of these types of photochemical reactions on aerosol oxidative aging and SOA formation.