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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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The aqueous phase that serves as a reaction medium in the atmosphere, is existing in the form of clouds, fogs, rain, and particulate matter consisting of either an aqueous solution containing pollutants or a film of water surrounding. Light-induced reactions facilitate the aqueous phase photochemical reactions. It is believed that light absorbing compounds such as photosensitizers in the atmospheric have a potential influence on the atmospheric aging, growth and formation of secondary organic aerosol (SOA). However, the kinetics, products, and mechanisms of the photosensitized reactions are still poorly understood. This study was aimed to investigate the photosensitized reactions of methyl vinyl ketone (MVK), methacrolein (MACR), and methacrylic acid (MCA by excited 2-IC (imidazole-2-carboxaldehyde) in the aqueous phase. Laser flash excitation-laser long-path absorption and ultra-performance liquid chromatography coupled with high-resolution electrospray ionization spectrometry were used to investigate their kinetics and reaction product(s), respectively. 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. Products related with the [2+2] cycloaddition of monomer and dimer of MVK to the excited carbonyl of 2-IC were observed. Similarly, a comparative study of the reaction between 3,4-dimethoxybenzaldehyde (DMB) as a photosensitizer and MVK were performed, and 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. This study has shown that cycloaddition of α, β-unsaturated carbonyl compounds to the excited triplet state of 2-IC or DMB potentially produced high molecular weight molecules in the atmosphere, which will provide potential insight to alleviate the discrepancy between measured and modelled results.