Photochemical properties of photosensitizers in tropospheric aqueous solution

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Abstract
Processes leading to the formation of secondary organic aerosols (SOA) are still poorly understood in atmospheric science (Ervens, 2011). Models based on available parametrizations of laboratory studies are strongly underestimating SOA masses and do not accord with the observed SOA masses from field studies (Hallquist, 2009). This discrepancy between ambient and modeled SOA concentrations suggests that other SOA sources and formation processes have not yet been identified and characterized. Recently, photosensitized particulate-phase chemistry is in discussion to be one of a missing process to SOA formation (Aregahegn, 2013; Monge, 2012; Rossignol, 2014). Such processes are known from other fields of science like surface water chemistry (Canonica, 1995; Canonica 2000), but little is known about such processes in/on atmospheric particles regarding to their kinetic and photochemical data as well as mechanisms of these photosensitized particle-phase reactions. However, the presence of photosensitizers like imidazole-2-carboxaldehyde in ambient aerosol particles (Teich, 2016) establishes an important new field of research of increasing activity.
In the present study, the photochemical behavior and properties of different photosensitizers like imidazole-2-carboxaldehyde (2-IC), 3,4-dimethoxybenzaldehyde (DMB), and 3-methoxyacetophenone (3-MAP) were investigated. Spectroscopic studies were carried out by laser flash photolysis-laser long pathway absorption (LFP-LLPA) to observe the formation of the excited triplet state of the photosensitizers at a specific time after the laser pulse (t_{delay} = 100 ns – 360 µs) resulting in a time-resolved absorbance spectra (λ = 200 – 800 nm). Additional, trapping reaction experiments were performed using LFP-LLPA to determine the quantum yields of the excited triplet state of the photosensitizers (ϕ_T(2-IC) = 0.9 at pH = 5 and T = 298 K). Hence, their absolute molar absorption coefficients from the above-mentioned absorbance spectra can be calculated. The received data will be included into further studies to evaluate the importance of particle-/aqueous-phase chemistry of photosensitizers for atmospheric processes as well as the impact of photosensitized reactions on atmospheric particles possibly contributing to SOA formation.
Keywords: photochemistry, multiphase chemistry, aqueous phase, photosensitization, quantum yield

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