Implications of Interfacial Photochemistry for Secondary Organic Aerosol Formation over Aquatic Environments

M. Brüggemann[1], P. A. Alpert[1], R. Ciuraru[1], F. Bernard[2], S. Rossignol[1], L. Tinel[1],
S. Perrier[1], Y. Dupart[1], D. J. Donaldson[3] and C. George[1]

[1] Université de Lyon 1 / CNRS, UMR5256, Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON), Villeurbanne, F-69626, France
[2] NOAA ESRL Chemical Sciences Division, 325 Broadway, R/CSD5 Boulder, CO 80305 USA
[3] Department of Chemistry, University of Toronto, 80 Saint George Street, Toronto, Ontario M5S 3H6, Canada

Keywords: multiphase chemistry, sea-surface microlayer, SOA, volatile organic compounds.

Presenting author email: martin.bruggemann@ircelyon.univ-lyon1.fr

Films of organic compounds exposed to the atmosphere are ubiquitously found on surfaces of cloud droplets, aerosol particles, buildings, plants, soils and the ocean. The sea-surface microlayer is one example of organic films that are host to countless biogenic amphiphilic compounds concentrated there with respect to bulk water. Yet, organic materials present in the bulk, such as humic acids and other photosensitizing compounds, can still have a tremendous impact on the surfactants (George, 2015).

Here, we present a laboratory investigation on secondary organic aerosol (SOA) formation from the reaction of ozone with volatile organic compounds (VOCs), originating from photo-induced processes in surfactant-containing water or sea-water. The results underscore the environmental importance of photochemical reactions at the air–water interface to produce SOA precursors in significant amounts, leading to significant particle formation and growth.

Laboratory experiments were conducted in a custom-built 2 m^3 Teflon reaction chamber with a pure or sea-water reservoir containing nonanoic acid, a model surfactant proxy for a surface microlayer, and humic acids when desired. In other experiments nonanol was used as a surfactant for comparison. VOC concentrations were measured over time using a proton transfer reaction–time of flight–mass spectrometer (PTR–ToF–MS) as a function of irradiation (UV and visible light) in a humidified low NO_x and low ozone environment. Additionally, photochemical gas- and liquid-phase products generated by irradiation of natural riverine biofilms were investigated. Characterization of organic compounds in water and aerosol particles was performed with ion chromatography and liquid chromatography–high resolution mass spectrometry (LC–HRMS) utilizing a quadrupole-orbitrap detector. Aerosol size distribution and numbers were continuously monitored during all experiments.

Production of VOCs occurred while the chamber air and water were irradiated with UV light for the nonanoic acid and pure water system. Gas-phase products included alkenes, aldehydes and dienes, as observed by PTR–ToF–MS in three different ionization modes (H_3O^+, NO^+ and O_2^+). Aerosol nucleation and growth occurred upon ozone introduction and reaction in the chamber but with lights switched off, further indicating the presence of unsaturated VOCs. Concentrations of aerosol particles were typically on the order of 10^2–10^3 cm^{-3}. When nonanoic acid and seawater were present, similar types and concentrations of VOCs were observed. Production of halogenated organic compounds was investigated using O_2^+ reagent ions. The addition of humic acids typically enhanced photochemical VOC production and aerosol formation, where SOA numbers exceeded 10^4 cm^{-3} after ozone injection and particle nucleation. We note that when nonanol was used as a surfactant, VOC and aerosol formation was never observed. This result highlights the potential importance of the carbonyl functionality of the acid group in the photochemical mechanism. The products were not only emitted to the gas phase, but also the bulk water. Using LC–HRMS the same VOCs, observed with the PTR–ToF–MS in the gas phase, were also identified in bulk water samples extracted during and after experiments. In addition, high molecular weight compounds such as highly oxidized organic molecules and molecular recombination products were identified in experiments with the nonanoic acid surfactant.

We suggest that light absorption precedes radical chemistry at the organic surfactant interface. Recent experimental findings in our group, supported by quantum chemical calculations, reveal the possibility of exciting nonanoic acid molecules to their triplet state even under irradiation of 300–320 nm wavelengths. Subsequent inter- and intra-molecular reactions have been proposed generating OH and other radicals leading to a suite of products. At an organic interface neighboring organic molecules are likely to react, especially in molecular layers such as those existing in organic or biogenic films. This proximity of organic molecules is unique to an interface, in contrast to the bulk or gas phase and thus, may also result in unique chemical reaction pathways leading to VOC formation. Fatty acid and organic compound coated surfaces are ubiquitous and photon-induced chemistry at organic interfaces may be important, ultimately influencing VOC flux and SOA formation at the Earth's surface and aloft.

References

George, C., Ammann, M., D'Anna, B. Donaldson, D. J., Nizkorodov, S. A. (2015), *Chemical Reviews* **115** (10), 4218–4258. DOI: 10.1021/cr500648z