

Photosensitized reactions at the air-sea interface: a potential source of aerosol

R. Ciuraru, F. Bernard, S. Rossignol, L. Fine, C. George

Université de Lyon, Université Lyon 1, CNRS, UMR5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, Villeurbanne, F-69626, France

FranceKeywords: multiphase chemistry, sea-surface microlayer, volatile organic compounds

Presenting author email: raluca.ciuraru@ircelyon.univ-lyon1.fr

The sea surface microlayer is the organic-enriched layer present at the air-sea interface which has different physical and chemical properties compared to subsurface waters. The chemical analysis of this microlayer is of great interest for many reasons including its major influence to reduce air-sea gas exchange by impeding molecular diffusion across the interface and by influencing the characteristics of water motion at the interface. Surface seawater contains a variety of substances which act as photosensitizers. They include components of the dissolved organic matter known also as humic acids. The sea surface microlayer is the primary recipient of the solar energy. Since the microlayer is enriched in chemicals and biota, a number of processes are likely to be more effective here than in the rest of the water column. These include changes in the chemical composition of the living cells of phytoplankton and the photodegradation of organic matter.

The focus of this study is to determine if the organic film acts as a hydrophobic barrier for the air-sea gas exchange and to identify and characterize the gaseous emissions and aerosol formation from the surface due to the photochemical processing of the sea surface microlayer. For this purpose, synthetic aqueous mixtures of NaCl, NaBr, NaI, photosensitizers (humic acids) containing an organic surfactant (hexanol, octanol, nonanoic acid) have been irradiated by means of a Xe lamp in a small Quartz cell. Potential gaseous products arising from this interfacial chemistry have been identified using a High Resolution Proton Transfer Reaction – Time of Flight Mass Spectrometer.

It has been observed that the presence of a thick organic film on the salt solutions reduces the transfer from the aqueous solution to the gas phase.

Experiments with an organic monolayer coverage at the air / interface led to the formation of a variety of gaseous aldehydes (heptanal, octanal, nonanal, nonenal), alkenes and -dienes (butene, 5-methyl-1, 4-hexadiene). All these compounds were confirmed by GC/MS analysis. A formation of methylglyoxal and acetylacetone has also been detected. Surprisingly, isoprene formation was also observed under irradiation. Isoprene is being made possible by a specific chemistry occurring solely at the air/water interface and the corresponding mechanism will be presented.

Experiments were also performed with benzophenone, imidazole and 2-imidazolecarboxyaldehyde as photosensitizers and the results will be discussed.

Furthermore, experimental studies in a 2m³ multiphase atmospheric simulation chamber will be presented. In this experimental approach, natural or artificial sea water containing a surfactant and a photosensitizer can be irradiated by UV/VIS lamps. But this tool is especially designed to follow the aerosol formation potential of the above mentioned photosensitized reactions at the air/water interface.

Indeed, the photochemical processing of the microlayer will lead to the emission of a series of functionalized VOC which will be measured using a PTR-ToF MS and a GC/MS. The chemical processing of a large subset of these VOCs will lead to the formation of Secondary Organic Aerosols. The physical and chemical properties of these particles will be monitored and characterized by means of a SMPS and an Orbitrap LC/MS measurements.

These results highlight the presence of an undocumented chemistry at the air/water interface having a real potential of affecting the budget of VOCs and SOA loading in the marine boundary layer.