

2.066 Probing the Role of Water in Criegee Chemistry Producing High Molecular Weight Compounds on Aqueous Organic Surfaces .

Early Career Scientist

Presenting Author:

Lijie Li, California Institute of Technology, saralilij@gmail.com

Co-Authors:

Agustín Colussi, California Institute of Technology

Shinichi Enami, National Institute for Environmental Studies

Michael Hoffmann, California Institute of Technology

Abstract:

Ozonolysis of unsaturated organic emissions is a fundamental process in the formation and growth of tropospheric aerosols. $O_3(g)$ reacts with alkenes producing reactive carbonyl oxide Criegee (Cl) intermediates via chemically activated ozonides. The competition among Cls reaction pathways determines the nature of the products formed and, hence, their impact on aerosol processing. In the gas phase, the fate of gas-phase Cls is dominated by their reactions with $(H_2O)_2$ clusters. The role of H_2O on Cls chemistry on the surface of the aqueous organic aerosols typically found in the troposphere, however, is not known. In this work, we report the products of H_2O reactions with the Cls generated in the ozonolysis of oleic acid (OL) at the aerial interface of water/acetonitrile (W/AN) solvent mixtures.

We focused on the formation of high molecular weight (HMW) compounds. Surface specific online electrospray mass spectrometry, which probes in situ within 1 ms the composition of the interfacial layers where ozonolysis takes place, was used to search for the α -hydroxy alkyl hydroperoxides (HAHP) (detected as Cl^- adducts) that would result from H_2O addition to Cls in competition with channels leading to C_9 and HMW ($\geq C_{18}$) organic species.

Major products were: α -acyloxyalkyl hydroperoxides (AAHP) from Cls reactions with OL itself, and C_9 -carboxylic acids from Cls isomerizations. There was no evidence of significant HAHP formation, which was confirmed in experiments using D_2O and $H_2^{18}O$ instead of H_2O in W/AN mixtures. In W/AN mixtures richer in H_2O , the formation of AAHP decreases likely due to the more extensive dissociation of OL into its inert carboxylate, indicative of an indirect role of H_2O in this system. Summing up: our findings suggest that H_2O does not compete with the formation of HMW compounds in the ozonolysis of OL at air-aqueous organics interfaces.