Experimental Report

07/03/2014

Proposal: **9-10-1287** **Council:** 10/2012

Title: Cloud water chemistry: does aqueous nitrate radical oxidse surfactantfilms

This proposal is a new proposal

Researh Area: Other...

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Samples: 1,2-distearoyl-sn-glycero-3-phosphocholine C44H88NO8P

Instrument	Req. Days	All. Days	From	To
FIGARO Langmuir trough	3	3	25/03/2013	28/03/2013

Abstract:

Projected modern atmospheric climate change is strongly influenced by clouds. The oxidative processing of pollutants in clouds affects droplet size and optical properties, important climatic effects. Clouds contain naturally occurring organic lipids forming organic films on the droplet. Oxidation and removal of this film can cause cloud evaporation or new cloud formation. Cloud droplets can occur in a glassy states at the top of the troposphere. In this work we will determine if the kinetics of thin film oxidation are affected by a glassy sub-phase. Specifically we will measure the rate of oxidation of oleic acid by ozone on viscous sub-phases: (1)glucose/water, (2) sulphuric acid/water and (3) conc. sea salt water and compare the determined rate constant to our published work on water. This exploratory work should result in a well-cited paper. The work will also support a STFC/NERC CASE award PhD students studies.

9-10-1287: Cloud water chemistry: does aqueous nitrate radical oxidize surfactant films?

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The experiment was a complete success, provided some excellent data and the results are being combined with those gained for the sulphate radical anion for publication. The work has provided two new piece of information that could only obtained from neutron scattering experiments:

1) **The thickness of the oxidized film decreases immediately – i.e. the film thins rather than holes**
2) **An atmospheric lifetime of thin films on clouds has been estimated**

Motivation

Clouds reflect solar radiation back to space and effectively cool the planet. The chemistry of the cloud droplet affects the activity and vapour pressure of water above the droplet. The atmosphere is a highly oxidising medium Thus atmospheric oxidation in cloud droplets can cause clouds to evaporate or retarding precipitation (rain) Aerosol and CCN have been shown to have a surface coating of organic molecules at the air-water interface. Surface active films on atmospheric aerosol (a) reduce the rate of evaporation from the particles, (b) inhibit the transport of chemicals from the gas to the liquid phase, (c) reduce the scavenging of the particles by larger cloud and ice particles.

In this proposal we investigated. for the first time, whether aqueous nitrate chemistry in a cloud droplet can oxidise a surface-active organic film at the air-water interface. By recording the kinetics of the oxidation reaction, we can calculate the atmospheric lifetime of the organic layer at the air-water interface and compare this to typical aerosol lifetime of 1-3 days. Thus if the chemical lifetime of the organic film with respect to oxidation by nitrate radical is less than 1-3 days the reaction is important and will be included in cloud microphysical models. The oxidation kinetics and products of the organic material at the air-water interface were probed by neutron reflection.

Experiment

We generated nitrate radicals in a null reflecting water sub-phase by the UV photolysis (λ=360nm) of a solution peroxydisulphate with excess nitrate anion. The photolysis is a 'clean' source of nitrate radicals with no complicated secondary or competing reactions. Photolysis allowed the radical chemistry to

be started and stopped so the kinetics can be matched to the acquisition time of FIAGRO. We used the lipid DSPC(1,2-distearoyl-*sn*-glycero-3-phosphocholine). A simple phospholipid with which we have experimental expertise and a good proxy for the surface active organic films from the sea-surface microlayer. We monitored the decay of surface coverage of deuterated material at the air-water interface (measured by neutron reflection analyzed using an Abeles routine), and from a temporal fit to a kinetic model, we determined the rate constant for initial nitrate radical attack.

Results

A typical kinetic run is demonstrated in the figure below. As can be seen the decay of the surface coverage of material is consistent with a chemical degradation process and we determined that three separate oxidation events are needed to completely remove a film molecule from the interface. Also, the film thickness for able to determined as a kinetic measurement. The film thickness thins from the start of the experiment demonstrating that thin thins, rather then holes – an important result for the cloud droplet microphysics modelling. The lifetime of the film with respect to nitrate radical reaction suggests the chemical processing off film by nitrate radical is slow relative to another ubiquitous atmospheric pollutant ozone, Another important atmospheric result.