Experimental Report

16/11/2012

Proposal:	**9-10-1192**	**Council:**	10/2011

Title: Arctic cloud chemistry: Can the Halogen "explosion" oxidise material at air-water interface of cloud droplets.

This proposal is a new proposal

Researh Area: Other

Main proposer: **KING Martin**

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Samples: CD3(CD2)16C(O)OH - Stearic acid

Instrument	**Req. Days**	**All. Days**	**From**	**To**
FIGARO Langmuir trough	3	3	12/11/2012	15/11/2012

Abstract:

The Arctic polar climate is strongly influenced by clouds. The oxidative processing of pollutants in Arctic clouds affects droplet size and optical properties, important climatic effects. Arctic clouds contain naturally occurring organic lipids forming organic films on the droplet. Arctic cloud chemistry unusually involves chlorine radical chemistry. Oxidation and removal of this film can cause cloud evaporation or new cloud formation. In this work we will study the kinetics of chlorine radicals with DPPC. Specifically we will (a) demonstrate that a common aqueous cloud oxidant, chlorine radical, can penetrate deep into the organic film and remove the film, (b) calculate the effect of the reaction on the hygroscopic properties of a cloud droplet and demonstrate removal of the organic film may cause a cloud to evaporate, (c) measure the kinetic rate constants for film oxidation and assess atmospheric relevance relative to ozone oxidation(d) Support a STFC/NERC CASE award PhD students initial studies.

Experimental report

No. 9-10-1192 (FIGARO)

Arctic cloud chemistry: Can Halogen “explosion” oxidize material at air-water interface of cloud droplets.

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This was an extremely successful experiment that successfully demonstrated that the halogen explosion in cloud water chemistry cannot compete with normal hydroxyl radical oxidation in cloud droplets. An important result for atmospheric science and will be written up for a peer reviewed publication. (Note the experiment was adapted from proposal as some of equipment for the experiment was seized by customs and delivered to ILL in time for

Motivation

The Arctic may be the most sensitive ecosystem to modern global climate change with strong atmosphere-ocean feedbacks.[1] Water clouds (as opposed to ice clouds) in the Arctic form above open leads in the sea-ice with biological organic matter from the ocean acting as cloud condensation nuclei.[2] Cloud formation and processing of the biological material will directly effect climate because clouds directly scatter solar radiation (cooling) and atmospheric oxidation indirectly changes the hygroscopiciticity and efficiency to act as cloud condensation nuclei (CCN). The biological CCN have lipids present as the film at the CCN air-water interface.[2] Surface-active organic films on aqueous 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 partcicles.[3] We have previously shown that chemical reactions in water droplets can have climatic effects.[4,5]

In this proposal we used neutrons to study the mechanism of an unusual Arctic atmospheric oxidant, atmospheric chlorine, *penetrating* and *reacting* within the lipid film itself. In sunlit Arctic atmospheres the oxidizing capacity of the atmosphere is greatly increased by chlorine (and bromine radicals) formed by the “halogen explosion” chemistry that liberates chloride from sea-water aerosol.[6] *We studied in detail whether the surface-active organic film at the air-water interface can be oxidized and removed by aqueous-phase by chlorine radicals.* The oxidation kinetics and products of the materials at the air-water interface was probed by neutron. The neutron work gave the molecular interpretation and kinetics.

Experiment

We generated chlorine radicals in a (null reflecting) water sub-phase by photolysis of 10% aqueous hydrogen peroxide in the presence of (0,0.5,1,1.5 and 2M) sodium chloride.[7] The OH radical, formed from the photolysis of H_2O_2, oxidizes the Cl^- present into chlorine radical anion, Cl_2^-. We used DSPC, a well-behaved lipid, that we have experimental expertise with, and a good proxy for surface-active organic films from the sea-surface microlayer.[2] The DSPC was completely deuterated (d75). We monitored the decay of surface coverage of deuterated material at the air-water interface (measured by neutron reflection and analyzed using an Abeles routine), and from a temporal fit to a kinetic model, we determined the rate constant for initial molecular chlorine radical anion attack.

It was expected that the molecular chlorine radical anion will penetrate into the tail region of the lipid and then react with the lipid removing a hydrogen atom to form HCl. A radical chain reaction will add oxygen to the lipid tail region and result in the lipid tail being broken and shortened in degradation kinetics. Several attacks by the molecular chlorine radical anion reduces the size of the lipid molecule to a soluble molecule that leaves the interface for the bulk solution. The extent and kinetics of this chemical process were previous unknown and were needed for atmospheric science.

Aims

1) Measure site-specific kinetic loss of DSPC at the air-water interface by molecular chlorine radical anions.
2) Elucidate whether the reaction of molecular chlorine radical anion with a saturated organic acid at the air-water interface removes the organic film from the interface. Neutron refection will allow composition and orientation of any new film to be determined.
3) Measure the oxidation rate by chlorine and assess atmospheric importance relative to other oxidants.

Results of preliminary work.

The Figure demonstrates the oxidation of DSPC with the molecular chlorine radical anions, along with the necessary blanks. The decay mechanism is not an exponential and the shape is characteristics of decay kinetics, i.e. A → B → C →D →E→... as opposed to A→ products. Initial fitting (not shown) demonstrates that five separate attacks and ensuing radical chain chemistry are needed to completely remove the molecule from the interface. Thus, as far as atmospheric science is concerned, the film resists oxidation and is likely to be important consideration in cloud atmospheric models. Initial analysis also revealed the surprise result that the oxidation appears to be controlled by the hydroxyl radical and not the molecular chlorine radical anion. This would initially suggest that the reaction rate constant is up to a factor of 10,000 slower than the reaction with hydroxyl radical. The photolysis chemistry was tuned to maintain a factor of 10,000 between the concentrations of the radicals. Thus an important result is that the aqueous-phase reactions of the molecular chlorine radical anion are not atmospherically important and need not be added to cloud models. Further work will now calculate the kinetics for the hydroxyl radical with DSPC.

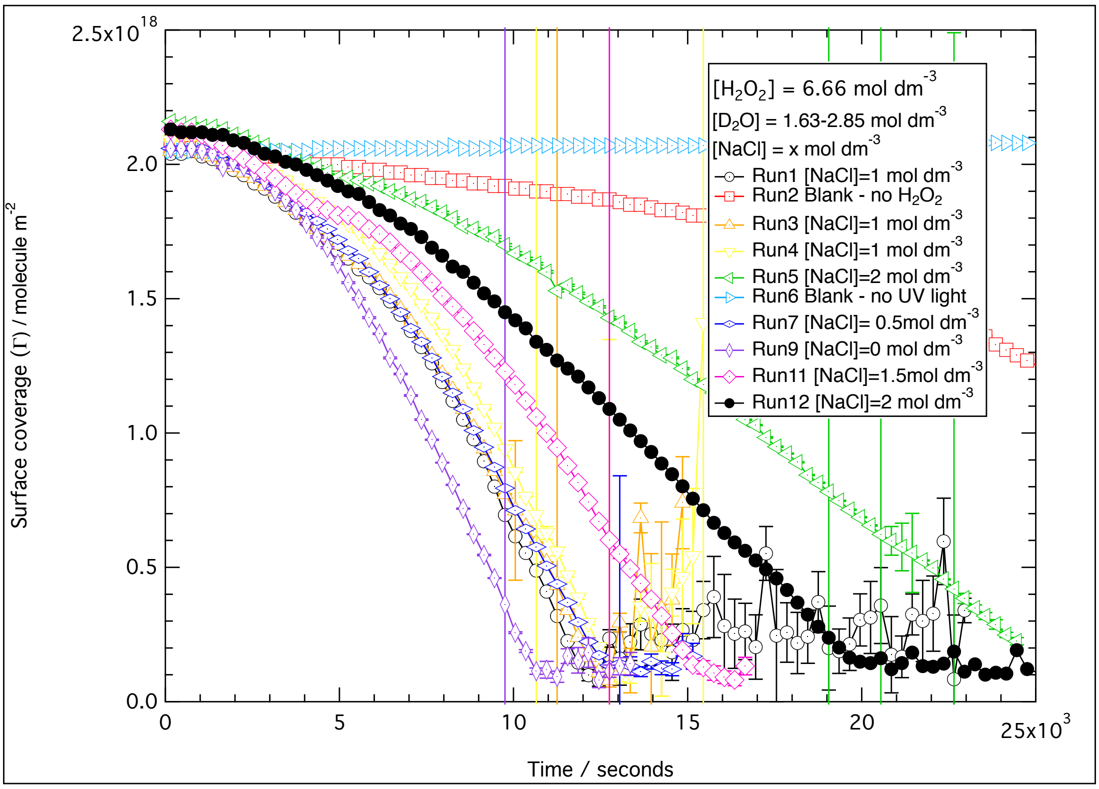

Figure: Surface coverage of DSPC as it is oxidized by hydroxyl radicals in the presence of unreactive chlorine radical. The reaction rate may be sensitive to the ionic strength that will be important for atmospheric reactions.

References

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