Experimental report

04/02/2016

Proposal:	**9-10-1187**	**Council:**	10/2011
Title:	Night-time Oxidation: Towards Multi-Reactive Model Systems Representative of Surfactant-Covered Atmospheric Aerosols		
Research area:	Chemistry		

This proposal is a resubmission of 9-10-1144

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Samples: d-oleic acid CD3(CD2)7CD=CD(CD2)7CO2D
d-stearic acid C18D35HO2
d-palmitic acid CD3(CD2)14CO2H

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	3	3	05/04/2013	08/04/2013

Abstract:

Organic layers on atmospheric aerosol strongly influence its behaviour. The rates and relative proportions of surface/bulk chemical reactions of these particles are hardly known and it is becoming apparent that mixed organic aerosol matrices may protect reactive species from oxidative degradation. While studies of monomolecular films provide first constraining parameters for atmospheric models, organic films on aerosols are present as multi-component mixtures and a simple extrapolation from mono- to multi-reactive films will introduce large uncertainties. As a part of ILLs NEATNOx studentship, we will lay the groundwork for the first studies of mixed films at the air-water interface using night-time oxidants. Kinetic studies of oleic, OA, stearic, SA, and palmitic, PA, acids in reaction with NOx will allow us to pin down the kinetics of these mono-reactive systems, so that we will be able to contrast kinetic parameters in future studies involving mixtures of OA, SA and/or PA. Complementing this proposal, we will use a kinetic model to predict the mixed film behaviour for OA/SA. Kinetic data on PA will allow the first model representation of oxidative ageing of ternary films by NOx

Experimental Report: Night-time Oxidation: Towards Multi-Reactive Model Systems Representative of Surfactant-Covered Atmospheric Aerosols

The behaviour of aerosols induces large uncertainties for the assessment of human contributions to climate change.[1] Clouds may reduce the radiation incident on the Earth's surface, increase solar heating, or suppress rainfall. The impact of cloud aerosol on the Earth's radiative balance and the formation of clouds is the largest uncertainty in assessing the effect of particulate matter on our climate.[2] Nearly all atmospheric aerosols are covered in surfactants or contain organic compounds that are often surface-active.[3] Organic layers strongly influence aerosol behaviour.[4]

Atmospheric oxidation is initiated by nitrate radicals, NO_3, hydroxyl radicals, OH, and ozone, O_3. Furthermore the night-time oxidant N_2O_5 has substantial impact on heterogeneous atmospheric chemistry and several studies have investigated its gas-phase behaviour.[5] The chemistry of the nitrogen oxides (NO_x) is important because of its role in photochemical ozone production, responsible for smog formation. The rates and relative proportions of surface/bulk chemical reactions of aerosol particles are hardly known and it is becoming apparent that the behaviour of mixed organic aerosol matrices may protect reactive species, such as oleic acid, from oxidative degradation.[6,7,8]

Moving towards multi-reactive model systems

While studies of monomolecular films are necessary starting systems to provide constraining parameters for atmospheric models, organic films on aerosol droplets are usually present as multi-component mixtures. Mixed films evidently behave differently to monomolecular films, so a simple extrapolation from basic studies will introduce considerable uncertainties in the description of atmospheric processes.[7] As a part of ILL's NEATNOx studentship project on FIGARO, we were planning to lay the groundwork for the first studies of mixed films at the air-water interface using night-time oxidants. Kinetic studies of oleic, OA, and stearic, SA, acids in reaction with NO_x will allowed us to pin down the kinetics of these mono-reactive systems, so that we will be able to contrast kinetic parameters in follow-up studies involving 50:50 mixtures of OA and SA. We used kinetic models based on previous work by the PI[6,7,8] to predict and model the mixed film behaviour for OA/SA. Given the very slow decay we found for SA, there was no time to study the decay of palmitic acid, PA, as originally intended.

Experimental Approach

N_2O_5 was produced in-situ using methodology developed for previous FIGARO experiments. $[N_2O_5]$ was varied by changing the relative flow rates of NO_2 and O_2 as well as the ozoniser settings. The new MIMIK chamber with a minimised volume of less than 0.5 L means that constant $[N_2O_5]$ was achieved in seconds. We investigated the mono-molecular films of OA, and SA in reaction with NO_x to obtain essential kinetic parameters for the subsequent study mixed films.

Experimental Results

Experimental results are presented in Figs. 1 and 2.

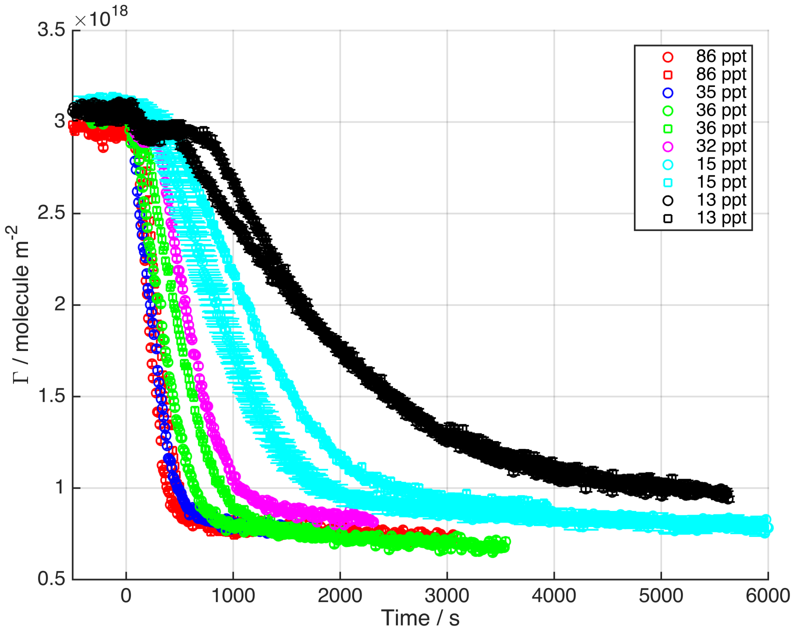

Figure 1: Surface excess decays of *d*OA exposed to different [NO_3]; mean values are displayed in the legend (1 ppt = 2.7 × 10^7 molecule cm^{-3}). NO_3 exposure is started at *t* = 0 s.

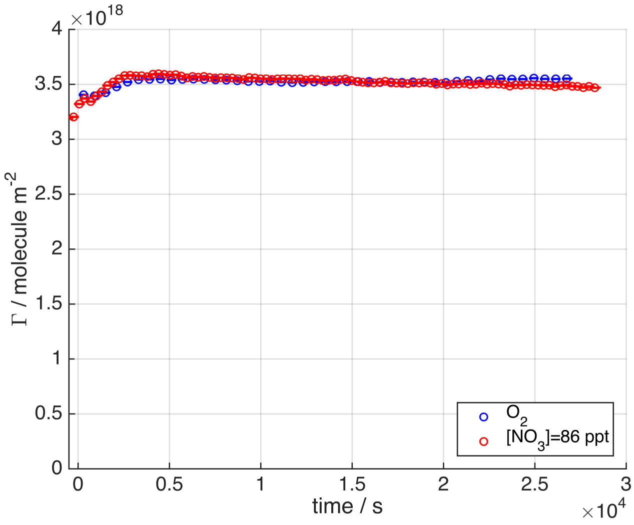

Figure 2: Surface excess of *d*SA exposed to O_2 (blue circles) and to [NO_3] = 86 ppt (red circles). Exposure to NO_3 starts at *t* = 0 s.

The results illustrated in Fig. 1 were kinetically modelled to determine the surface rate coefficient for NO_3-initiated oxidation of oleic acid. The experimental data presented in Fig. 2 allowed us to derive an upper limit for a rate coefficient for the much slower reaction of SA. Together with previous work, we were thus able to establish the importance of the chemical identity of the surfactant for kinetic parameters as well as for the film-forming potential of products.

This research is currently being written up for publication.

References [1] Shindell, D. T., *et al.*, **2009**, *Science*, 326, 716; Stevens, B. and G. Feingold, **2009**, *Nature*, 461, 607 // [2] IPCC, *Climate Change 2007: The Physical Science Basis,* **2007**, CUP // [3] Fuzzi, S., *et al.,* **2006**, *Atmos. Chem. Phys.*, 6, 2017 // [4] King, M.D., Rennie, A.R., Thompson, K.C., Fisher, F.N., Dong, C.C., Thomas, R.K., Pfrang, C. and Hughes, A.V., **2009**, *Phys. Chem. Chem. Phys.*, 11, 7699 // [5] Brown, S.S., *et al.*, **2006**, *Science*, 311, 67; Pfrang, C., *et al.*, **2006**, *Phys. Chem. Chem. Phys.*, 8, 354; Pfrang, C., *et al.*, **2007**, *Atmos. Environ.*, 41, 1652 // [6] Pfrang, C. et al., **2010,** *Atmos Chem Phys*, 10, 4537 // [7] Pfrang, C. et al., **2011**, *Atmos. Chem. Phys.*, 11, 7343 // [8] Shiraiwa, Pfrang and Pöschl, **2010**, *Atmos. Chem. Phys.*, 10, 3673.