Experimental report

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Proposal: **9-10-1234** **Council:** 4/2012

Title: New Model for Atmospheric Surfactants: Chemical Ageing of PalmitoleicAcid.

Research area: Chemistry

This proposal is a new proposal

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Samples: d-palmitoleic acid ($C16D29HO2$)

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	3	3	25/06/2013	28/06/2013

Abstract:

Surfactants are omnipresent in the atmosphere and are very likely to alter properties of aerosols which are of key importance for our climate. Palmitoleic acid, POA, is recognised to be one of the most abundant unsaturated surfactants and an important tracer for meat cooking emissions. Despite being detected at comparable atmospheric concentrations to the popular model surfactant oleic acid, POA and its oxidative ageing has not been examined in any detail. We propose the first kinetic study at the air-water interface on FIGARO of this surfactant as a new model for atmospheric aerosols using key atmospheric oxidants (ozone and nitrogen oxides). This study will establish the importance of the chemical identity of the surfactant for kinetic parameters as well as for the film-forming potential of products. As interfacial processes can vary widely even for closely related precursors such as oleic and palmitoleic acids, this experiment lays the foundation for future work on mixed systems as more realistic models for relevant atmospheric processes. d29-POA will be custom-synthesised for this experiment by the Oxford Deuteration Laboratory.

Experimental Report:
New Model for Atmospheric Surfactants: Chemical Ageing of Palmitoleic Acid.

Surfactants are omnipresent in the atmosphere and very likely to alter properties of aerosols which are of key importance for our climate.[1] Chemical identification of atmospheric surfactants is often ambiguous (e.g. aerosol mass spectrometry studies only identify functional groups or characteristic fragments and not definite chemical identities),[2] but oleic, palmitoleic and cetoleic acids are recognized to be the most abundant unsaturated surfactants.[e.g. 3] Unsaturated fatty acids are known to be released by microbial sources and processing, degradation and combustion of vegetable and animal materials.[4] Rogge et al. (1991)[5] showed that food is an important source for palmitoleic acid, POA, in particular cooking with seed oils or margarines. POA is important as marker specifically for meat cooking aerosols since oleic acid originates from a range of sources not exclusively associated with meat cooking.[6]

While oleic acid has been used as a model system for atmospheric surfactants for decades, [e.g. 7 and references therein] studies of POA -detected at comparable atmospheric concentrations-[e.g. 3] and its chemical ageing are very sparse. POA has been recognized as a tracer and model compound for meat cooking emissions[6,8] and it is likely to play a role for phase changes and thus reduced diffusivity in multi-component semi-solid atmospheric aerosol matrices.[9] Formation of such highly viscous and semi-solid aerosols in the atmosphere has recently been demonstrated,[10] but its mechanism is very poorly understood at present. The behaviour of POA at the air-water interface has not been investigated at all despite its potential importance. This proposal aims to provide a first step to remedy this shortcoming. It is becoming apparent that limiting studies to one model surfactant is far too simplistic to provide a fundamental understanding of the processes occurring in the complex organic aerosols present in the atmosphere.[e.g. 8] In particular the processes at the air-water interface are strongly dependent on the relative speeds of the processing by the key atmospheric oxidants as well as on the properties of reaction products, in particular film-forming potential and volatility. These properties can vary widely even for closely related precursors such as oleic and palmitoleic acids.

Unsaturated fatty acids will be oxidized by the initiators of atmospheric oxidation NO_3, O_3 and OH. Reactive oxygen intermediates involved in the reactions of ozone with aerosol particles have recently been shown to play an important role in both atmospheric chemistry and physiological processes.[11] Furthermore, the key importance of nitrogen oxides like NO_2 and NO_3 as reactive nitrogen species has been recognized.[12] The proposed study will focus on the POA oxidation by ozone and nitrogen oxides. The first set of experiments will investigate the POA oxidation by varying concentrations of ozone in oxygen. We will then study POA reactions with NO_3 in presence of varying concentrations of the less reactive nitrogen oxides NO_2 and N_2O_5.

Experimental Approach

Ozone was generated in a flow of oxygen using a commercial pen-ray ozoniser at ppb-ppm levels. 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 concentrations of ozone or nitrogen oxides were now achieved in seconds. We investigated mono-molecular films of POA in reaction with nitrogen oxides to establish essential kinetic parameters as well as the film-forming potential of reaction products.

Experimental Results

We conducted the first kinetic study at the air-water interface of a new model surfactant for atmospheric aerosols (see Fig. 1).

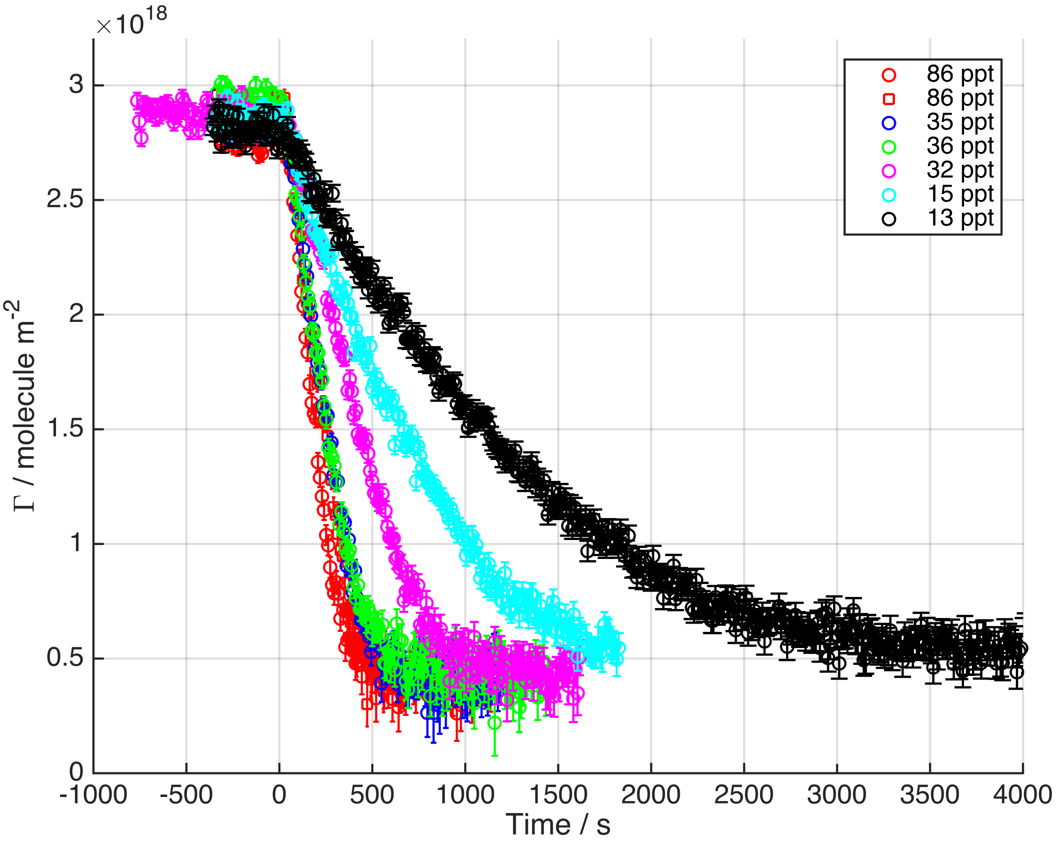

Figure 1: Surface excess decays of *d*POA exposed to different [NO_3]; mean values are displayed in the legend. NO_3 exposure is started at *t* = 0 s.

The experimental data presented in Fig. 1 allowed us to determine the surface rate coefficient by using kinetic modelling. This extended the knowledge base of surface reactivity of atmospheric surfactants and established 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] Stevens, B. and G. Feingold, **2009**, *Nature*, 461, 607; Ziemann, P. J., **2009**, *Nature*, 461, 353; IPCC, *Climate Change 2007: The Physical Science Basis,* **2007**, CUP; Fuzzi, S., *et al.,* **2006**, *Atmos. Chem. Phys.*, 6, 2017; Lohmann, U. and Feichter, J., **2005**, *Atmos. Chem. Phys.*, 5, 715 // [2] Allan, J. D., *et al.*, **2010**, *Atmos. Chem. Phys.*, 10, 647 // [3] Lichtfouse, E., Schwarzbauer, J., Robert, D., *Environmental chemistry: green chemistry and pollutants in ecosystems*, Springer, **2005**, ISBN 3540228608, p. 377 // [4] Rogge, W. F., *et al.*, **1993**, *Atmos. Environ.*, 27, 8, 1309 // [5] Rogge, W. F., *et al.*, **1991**, *Environ. Sci. Technol.*, 25, 6, 1112 // [6] Shrivastava, M. K., *et al.*, **2007**, *Atmos. Environ.*, 41, 9353 // [7] 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 // [8] Huff-Hartz, K. E. H., *et al.*, **2007**, *J. Geophys. Res.-Atmos.*, 112, D04204, doi:10.1029/2006jd007526, // [9] Pfrang *et al.*, **2011**, *Atmos. Chem. Phys.*, 11, 7343 // [10] Virtanen, A., *et al.*, **2010**, *Nature*, 467, 824 // [11] Shiraiwa, M., *et al.*, **2011**, *Nature Chem.*, 3, 291 // [12] Finkel, T. and Holbrook, N. J., **2000**, *Nature*, 408, 239.