Experimental report

05/02/2016

Proposal: **9-10-1344** **Council:** 4/2014

Title: Completion of work on night-time oxidation. Towards a model closer toreality: mixed organic films.

Research area: Chemistry

This proposal is a continuation of 9-10-1286

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Samples: d-oleic acid CD3(CD2)7CD=CD(CD2)7CO2D
d-methyl oleate CD3(CD2)7CD=CD(CD2)7CO2CH
h-stearic acid
h-methyl oleate
h-oleic acid

Instrument	Requested days	Allocated days	From	To
FIGARO User-supplied	4	4	04/09/2014	07/09/2014

Abstract:

Quantifying amount, composition and fate of surface-active organic aerosols originating from cooking processes is a key atmospheric research activity. Our project aims to investigate the oxidation of organic-coated aerosols, particularly for the key night-time oxidant NO3. By carrying out experiments on single components, we learnt that the surface tension drops much faster than the surface excess, thus it is not possible to relate them satisfactorily. The next step is to move to more realistic models for cooking aerosols, studying the binary mixtures of the three previously investigated surfactants. We will study the two unsaturated surfactants methyl oleate and oleic acid and three binary mixtures (including saturated stearic acid) exposed to NO3. This will allow us to understand how the interaction between the two components affects the oxidation reaction, its rate coefficient and the product fate.

Experimental Report:
Completion of work on night-time oxidation. Towards a model closer to reality: mixed organic films.

Scientific Interest

In the last decade many aerosol scientists focused their efforts on quantifying the amount of organic aerosols emitted due to cooking processes and on determining their composition and properties [e.g. Zhao et al. 2007, Mohr et al. 2012]. Hundreds of organic compounds have been found, some of them are carcinogenic and mutagenic, some can impact on atmospheric chemical processes, and all particles may have a large influence on solar radiation. Many field and laboratory measurements investigate the various life stages of an organic aerosol particle. The processes that transform primary organic aerosols into oxidised aerosols are poorly understood, in particular the processes occurring at the aerosol surface.

Our Interest and previous studies

Our project aims to investigate the oxidation of organic coated aerosols, particularly focussing on night-time oxidation by nitrate radicals, NO_3. NO_3 is one of the key atmospheric oxidants and its impact on surfactant ageing is not yet well described. Previously, we studied three organic surfactants separately: oleic acid (OA) [Sebastiani et al. 2012], stearic acid (SA) [Report #9-10-1143] and methyl oleate (MO) [Report #9-12-260; Pfrang et al., 2014; Sebastiani et al., 2015]. The analysis of the rate coefficients suggests that OA and MO show fairly similar rate coefficients whereas SA shows a much slower decay. The next step for the NEATNOx project was to move to a more realistic model for cooking aerosols, i.e. studying binary mixtures of the three previously studied surfactants. The aim was to understand how the interaction between the two components affects the oxidative decay and to determine the relative rate coefficients. By carrying out experiments on single components, we learnt that the surface tension drops much faster than the surface excess, thus it is not possible to relate them satisfactorily. Thanks to the experiments already performed, we know that it is fundamental to have unequivocal information on the end of the reaction, because it provided us insights on the reaction mechanism as well as on possible products formation, and it helped us refine the kinetic models applied to analyse the data.

Preliminary work has been performed on these mixtures by Brewster angle microscopy: (i) the system SA/OA is non-mixing as expected (clear domains, indicated by bright reflections of the laser beam), because of the different saturation states of the chains. This will be our baseline system where we might expect that the rate coefficients compared with those for the pure systems are only minimally affected due to the lesser molecular interactions between the components; (ii) the SA/MO and OA/MO systems exist in mixed states. These should allow us to quantify the effects on the rate coefficients from mixing on the molecular level.

Experimental Approach

Nitrous oxides were generated using the same protocols as in our previous FIGARO experiments (e.g. see experimental reports #9-12-170 and #9-11-1143). The new MIMIK chamber with a volume of less than 1 L means that constant concentrations of nitrogen oxides were achieved in seconds thus reducing gas mixing effects. The SA/OA, SA/MO and OA/MO monolayers in reaction with nitrogen oxides were studied in order to establish essential kinetic parameters as well as the film-forming potential of reaction products. We used d35-SA and d34-OA, available commercially, and new supplies of deuterated MO, provided by the Oxford Deuteration Facility.

Experimental Results

We studied the three binary mixtures (1:1) SA/OA, SA/MO and OA/MO exposed to NO_3. The following reactions were studied: the decay of deuterated OA with hydrogenated SA, deuterated MO with hydrogenated SA, and then deuterated OA with hydrogenated MO; both OA and MO react fast enough to be studied in the same mixtures whereas the relative decay of SA was too slow to see if the rate coefficient has changed significantly. The experimental results for the binary mixtures of dMO/hSA and dOA/hSA are presented in Figs. 1 and 2, respectively.

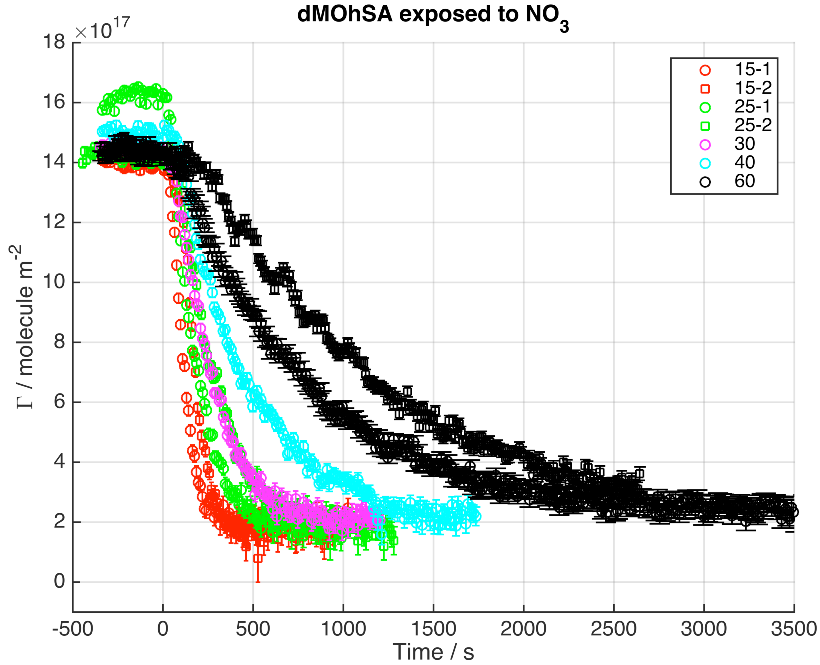

Figure 1: Binary mixture (1:1) of dMO and hSA exposed to a range of $[NO_3]$.

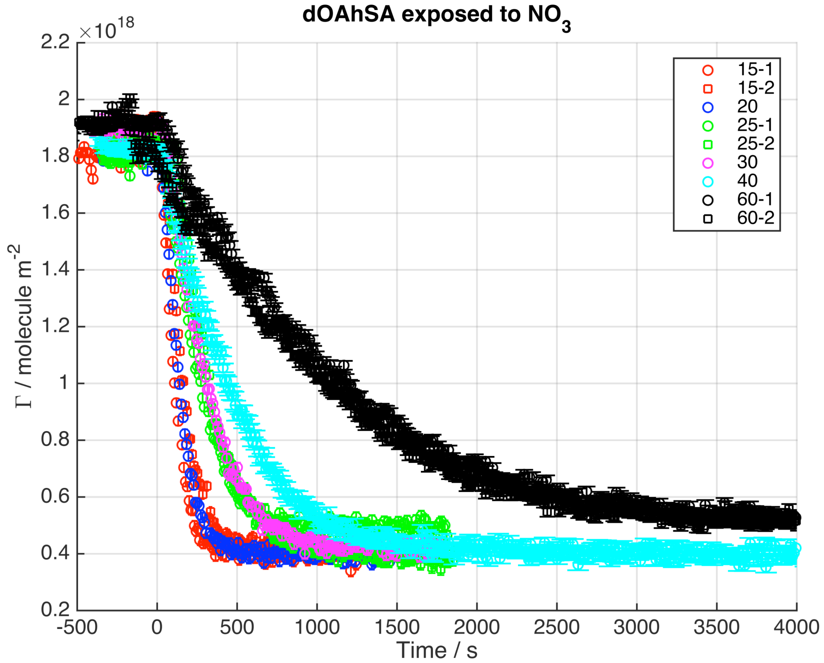

Figure 2: Binary mixture (1:1) of dOA and hSA exposed to a range of $[NO_3]$.

We are currently completing the model analysis to establish the mixed rate coefficients for MO and OA in the presence of SA, as well as for MO and OA in presence of each other.

This work is being written up for publication.

References

Mohr, C. et al., 2012, Atmos. Chem. Phys., **12**, 1649–1665 ; Pfrang, C. et al., 2014, Phys. Chem. Chem. Phys., **16**, 13220–13228; Sebastiani, F. et al., 2012, Poster EAC2012; Sebastiani, F. et al., 2015, *RSC Adv.*, **5**, 107105–107111; Zhao, Y. et al., 2007, Environ. Sci. Technol., **41**, 99–105.