Experimental report

04/02/2016

Proposal: 9-10-1233 **Council:** 4/2012

Title: Fast Neutron Reflectometry for Study of Oxidation of Poly-UnsaturatedFatty Acids

Research area: Chemistry

This proposal is a new proposal

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Samples: d8-arachidonic acid (CH3(CH2)4(CD=CDCH2)4CH2CH2CO2H)

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	4	3	31/05/2013	03/06/2013

Abstract:

Arachidonic acid (AA) is the most common unsaturated fatty acid in cellular membranes and recent evidence suggests that its increased intake may contribute to the rise in allergies in the Western World. AA will partition to the surface of aqueous droplets and thus be exposed to gas-phase atmospheric oxidants. The fast-kinetics capability of our newly commissioned MIMIK chamber will be exploited to study the oxidation of d8-AA which recently became commercially available. We will investigate its oxidative ageing in reaction with ozone and nitrogen oxides at the air-water interface for the first time. Development of fast kinetics is a distinct part of the ILL-based NEATNOx studentship. We propose the first kinetic study of a poly-unsaturated surfactant in a step towards a more realistic representation of atmospheric aerosols with multiple reactive sites. The experimental work in conjunction with the kinetic modelling interpretation will allow tentative extrapolation to atmospheric conditions. This research will showcase FIGARO as the premier instrument for fast kinetic studies and climate change science.

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Preambel:

For this beam time we focussed on characterisation and application of the newly commissioned MIMIK reaction chamber for fast kinetics. We completed the study of ozonolysis of methyl oleate and carefully characterised flow and mixing conditions. We decided that this was the better system to ensure suitable signal-to-noise ratios given that we could not obtained sufficiently highly deuterated arachidonic acid (AA) in time for this beam time to ensure a strong neutron signal. As proposed, we harvested the newly developed fast kinetic capability enabling us to study fast reactions.

Experimental Approach/Results

Ozone was generated in a flow of oxygen using a commercial pen-ray ozoniser at ppb-ppm levels. The new MIMIK chamber with a minimised volume of less than 0.5 L means that constant concentrations of ozone were achieved in seconds. We investigated mono-molecular films of methyl oleate in reaction with ozone to establish essential kinetic parameters as well as the film-forming potential of reaction products.

The development of the MIMIK chamber was a distinct part of the ILL-funded NEATNOx studentship and this part was successfully completed with this beam time experiment.

The results of the characterisation of the flow conditions in the MIMIK chamber are presented in Fig. 1.

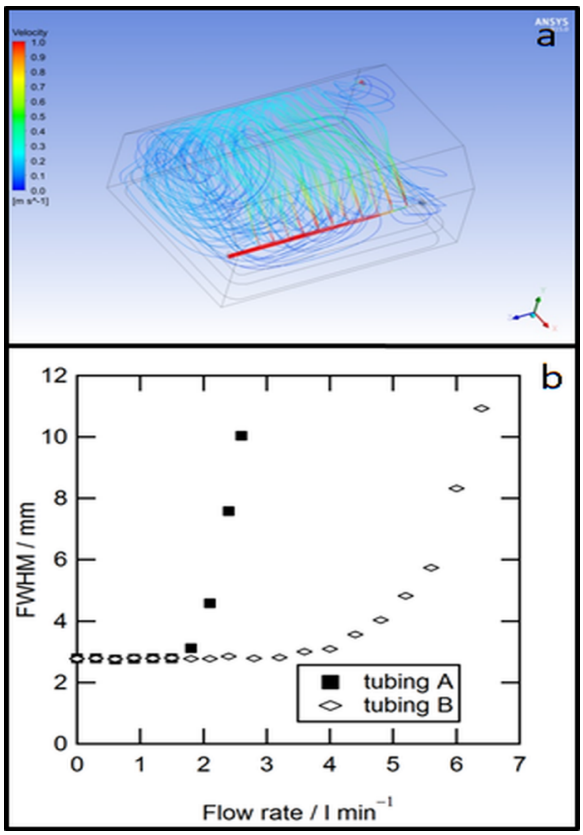

Figure 1: a. Ray tracing image of the velocity profile in the reaction chamber when simulating a flow of pure O_2 at 25 °C and 5 l min^{-1}. b. Width of the peak corresponding to the specular reflection of neutrons at a clean air–D_2O interface with respect to the flow rate through the reaction chamber. Two different inlet systems were employed: tubing A with 11 holes of 1-mm diameter (black squares) and tubing B with 11 holes at 2-mm diameter (white diamonds). Tubing A was used at a flow rate of 1.8 l min^{-1} for all the ellipsometry studies while tubing B was used at the max. flow rate of 5 l min^{-1} for NR.

The kinetic experimental neutron data obtained are presented in Fig. 2.

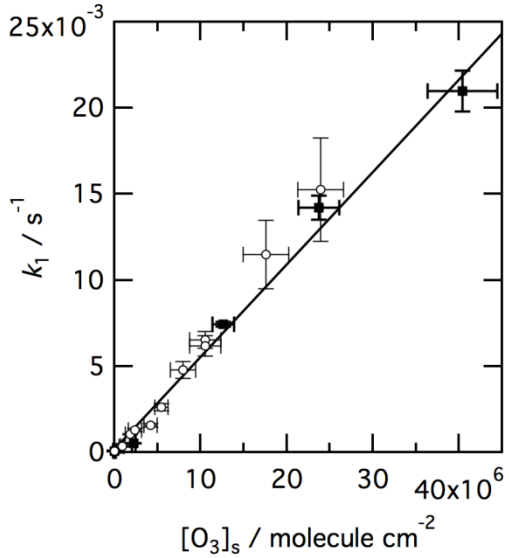

Figure 2: Pseudo–first order rate coefficients, k_1, as a function of the ozone surface concentration, $[O_3]_s$, for methyl oleate monolayers measured using NR in the new reaction chamber (black squares) and those reported previously in a large chamber (white circles). The error bars represent the associated uncertainties at one standard deviation. The solid line corresponds to an orthogonal distance regression fit weighted by the uncertainties both in k_1 and $[O_3]_s$ using only the four new data points. The small positive intercept lies well within the uncertainty of the fit ($(2 \pm 7) \times 10^{-4}$ s^{-1}).

This work has been now published in *RSC Advances* (Sebastiani, F., Campbell, R. A. and Pfrang, C., *RSC Adv.* 2015, **5**, 107105).