Experimental report

19/06/2019

Proposal:	**9-10-1518**	**Council:**	4/2017

Title: Oxidation Kinetics of Oleic Acid in Mixed Fatty Acid Monolayers: Miscible Vs Immiscible Mixtures.

Research area: Chemistry

This proposal is a continuation of 9-10-1344

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Samples:
h-stearic acid
h-palmitoleic acid
d-stearic acid (CD3(CD2)16CO2H)
d-oleic acid (CD3(CD2)7CD=CD(CD2)7CO2H)
d-palmitoleic acid (CD3(CD2)5CD=CD(CD2)7COOH)

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	4	3	02/07/2018	05/07/2018

Abstract:

Fatty acid films at air-water boundaries modify the surface properties of water droplets, affecting cloud formation, and act as adsorption surfaces and/or mass transport barriers. These films are aged by atmospheric oxidants such as nitrate radicals (NO3). The kinetics of these reactions are different from those seen for gas-phase or bulk reactions.

Current work explores how multi-component films differ from single-component films. Initial results suggested that oleic acid (OA) reacts more slowly with NO3 when stearic acid (SA) is present, but not when methyl oleate (MO) is co-deposited; recent work at ISIS has revealed that selective deuteration can affect measurements of surface coverage in immiscible mixed films (such as OA/SA, but not OA/MO). This calls into question the finding that OA reacts more slowly with NO-3 when SA is present; this needs to be resolved before publication of the ILL work.

The proposed work will test this hypothesis & provide more reliable kinetic parameters for the OA/NO3 reaction in SA presence. We will study a miscible system (OA/palmitoleic acid (POA)) to further confirm our hypothesis and determine the kinetics of the OA/NO3 system in POA presence

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This experiment is part of an series of experiments on FIGARO and INTER (at ISIS) designed to probe the effects of temperature and subphase salinity on the oxidation by O_3 of oleic acid (OA) monolayers at the air-water interface. This experiment focused in particular on investigating differences in kinetic parameters for the oxidation on a pure water subphase between room temperature and a more atmospherically realistic near-freezing temperature, as well as on elucidating the threshold temperature at which a product monolayer is retained at the interface after oxidation.

The bulk of the experiment consisted in oxidising OA layers with O_3 at various different concentrations in a dry O_2 stream, first at room temperature, and then at 3°C. An example of this sort of experiment is shown in Figure 1.

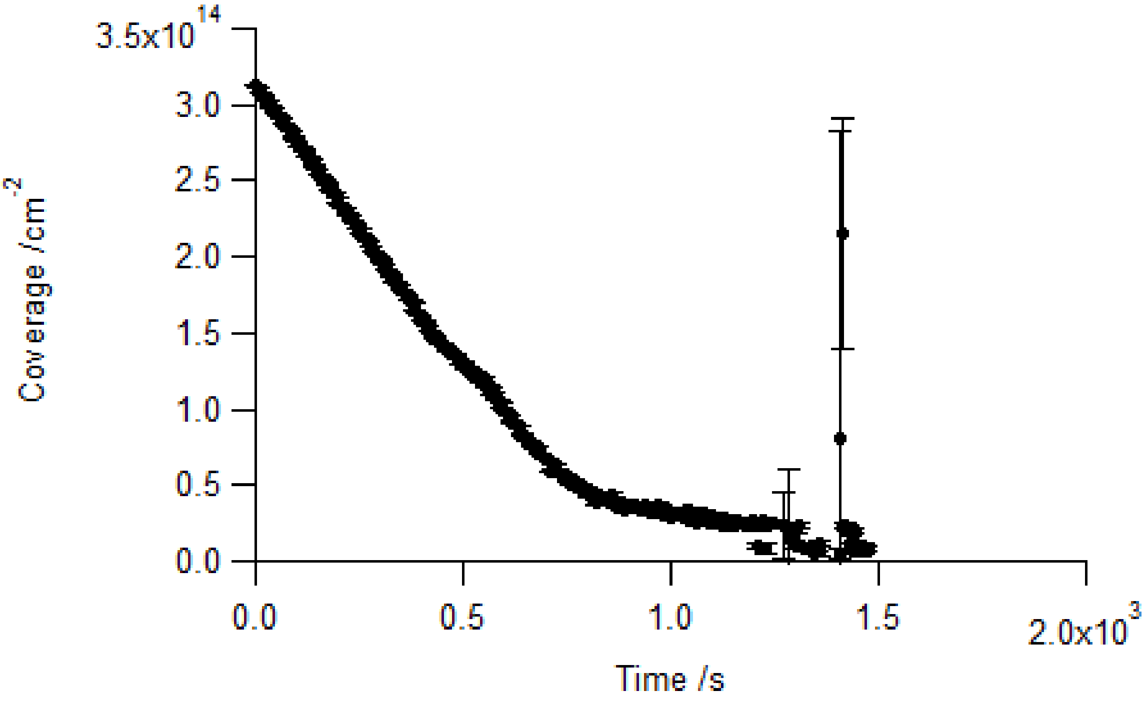

Figure 1 – Oxidation of OA on pure water by O_3, $[O_3]$ = 126 ppb); T = 20°C

These decays were fitted to a modified exponential model developed preciously by this group in which the pseudo-first-order decay induced by an excess of O_3 is combined with an exponential that describes the mixing of O_3 into the reaction chamber. This does not describe the first few seconds of the reaction, nor the latter stages (where the partitioning of products is uncertain), but is fitted to the middle period of these decays (from 15s after the start of the reaction until the fitted OA surface coverage drops to 10^{14} cm^{-2}) to give pseudo-1st-order rate constants for each $[O_3]$ value. Surface $[O_3]$ is calculated from gaseous $[O_3]$ using Henry's Law. These fitted pseudo-1st-order rate constants are plotted against $[O_3]_{surf}$ and the gradient of the line gives a 2nd-order rate constant for the reaction. This showed that the rate of this reaction does not vary substantially (more than 10%) between these two conditions. This is in line with previous studies on the heterogeneous reaction between O_3 and liquid OA. The threshold at which a product monolayer remains at the interface was studied using a temperature ramping experiment. The crossover point for stability of the product monolayer was identified to be in the range 7-11°C, which is the range at which the product distribution from the OA/O_3 reaction has been observed to shift in other studies.