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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ozonolysis of fatty acid monolayers at the air–water interface: organic films may persist at the surface of atmospheric aerosols" *by* Ben Woden et al.

Anonymous Referee #2

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The authors present studies of the interfacial composition of aqueous substrates containing oleic acid that have been exposed to ozone. This reaction has been studied extensively in the past using measurements of loss of ozone or oleic acid, but more recent measurements have attempted to study the chemical composition of the interface itself. This paper uses primarily neutron reflection and some infrared reflection measurements to do this. The experiments appear to have been well done (although I am not a neutron reflection expert) and the results have good reproducibility. Some of the work has been done with ozone mixing ratios approaching atmospheric values. The paper is relatively clear but I reinforce the comments from the previous reviewer that it is much more wordy than it needs to be. I think the results/discussion could be

shortened by at least 1/3 without any loss of content. The major results are that the lowest temperatures on the salt films support an organic film after reaction whereas higher temperatures do not, and that the kinetics of oleic acid loss are temperature independent over about 20 C temperature change.

Comments:

1. The experimental apparatus should be shown as a schematic. In particular, I could not tell whether ozone is constantly flowing or added in a batch mode. What is the chamber made of? Where is the ozone measured, i.e. before or after the surface? Could changes of ozone mixing ratio be used to monitor the reaction? What was the surface area of the substrates? How was oleic acid added to it? How was ozone generated? Was there NOx present? Is the experiment done in air or nitrogen? Was the air preconditioned to 100% RH or is the substrate evaporating all the time? Does substantial evaporation occur over the timescale of the experiment? Is the oleic acid a sub-monolayer coverage? What is the coverage? Essentially, enough detail should be provided that someone else could reproduce the main elements of the experimental design; I don't think that is possible now.

2. The mechanistic understanding of the ozone – oleic acid reaction (i.e. four products formed as shown in the reaction scheme) is a conventional one. In the past few years, it has been reported that the Criegee intermediate does not only rearrange to form a carboxylic acid. Rather, it also reacts with protic reactants, including carboxylic acids. The product is a hydroperoxide ester. See a number of papers by Enami/Colussi for reactions at the air-water interface (e.g. PCCP, 2017 with pinonic acid); also, see the work by Zhou et al., ES&T Letters, 2019. And so, I don't think it is safe to conclude that the simple four products presented are the only possible products given the potential for secondary chemistry. Studies as a function of oleic acid surface coverage could potentially disentangle this chemistry, i.e. show evidence for the Criegee intermediate reacting with oleic acid. Were experiments of this type done? Is there any evidence that the nature of the film changes as the amount of oleic acid on the film decreases?

3. The results as a function of temperature are not surprising, i.e. molecules are less volatile at lower temperatures, but this is the first study that shows this behavior for interfacial products in this reaction. Can the authors estimate the volatility of the assumed products from their measurements?

4. Following from point 3, only with volatility measurements can an accurate statement about atmospheric implications be made. Presently, the statements in the paper are incomplete and potentially wrong. While I agree that a surface film does remain in these experiments at low temperature, will it remain on the surface atmospheric conditions? This depends on the volatility of the products, the partial pressures of those species in the atmosphere, the amounts on the surfaces, and time. Essentially, for how long would the film exist on the surface in the atmosphere in the absence of new product formation and low partial pressures in the gas phase? Given enough time, everything will eventually evaporate! Is the film only stable at low temperatures because there are high partial pressures of the products in the gas phase in the reaction chamber which are stabilizing it?

5. The lack of temperature dependence in the ozone – oleic acid system has previously been shown by Thornberry and Abbatt, PCCP, 2003.

Overall, this is a solid study and I recommend its publication when the above points are addressed. It provides new measurements of thin layers of oleic acid on water surfaces, which is an important mimic for atmospherically important reactions. My major advice is to be much more careful with the atmospheric implications made and the potential products forming.

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