

Interactive comment on “Night-time oxidation of surfactants at the air–water interface: effects of chain length, head group and saturation” by Federica Sebastiani et al.

Anonymous Referee #1

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In this work the authors explore the oxidation of unsaturated surface active organic molecules (and one saturated organic molecule) by NO_3 radicals. They report data using neutron reflectometry and show the decay of signal with increasing reaction time. Kinetic models were applied to infer oxidant concentrations and to interpret the observations in light of a series of surface and near-surface processes. The investigation is interesting and has some relevance to oxidative processing of films on the ocean surface, aerosol particles and cloud droplets. In the current version of the manuscript, some severe limitations exist that call into question the usefulness of the kinetic parameters. I hope that in addressing the points below the authors can provide a more compelling description of their work and the validity of their conclusions.

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Main points:

- 1) The methodology associated with preparing the film should be detailed in the main text.
- 2) As far as I can tell, the compression of the film for the oxidation experiments is not reported anywhere. Please amend or make this information more prominent in the main text.
- 3) A more basic introduction to the NR technique is necessary, focusing on the observed quantities and what this actually means in these experiments. Where does the value of 'd' come from? Does 'd' change during an experiment in which shorter chain surface active species may be created, and how is this accounted for?
- 4) Uptake of N_2O_5 into aqueous phases can lead to acidification as HNO_3 is formed. How does the pH of the aqueous sub-phase change during the measurements, and how might changes in pH affect the film properties? Could changes in pH contribute towards the plateau observed in the initial time during some measurements? Might there be competition between uptake of N_2O_5 and NO_3 ?
- 5) It is not clear what assumptions are made in order to derive the rate constants. In particular, the authors should perform a sensitivity analysis to see how changes in branching ratios affect the results.
- 6) Looking at the data for OA vs POA, the uptake coefficients are similar, but the time constants are a factor of 2 different. What causes this? There appears to be no relation to NO_2/NO_3 adsorption lifetimes and uptake, so what purpose do they serve in the model? How would a change in adsorption lifetime manifest itself in the experimental data or the parameters they pull out?
- 7) What would the decay curves look like if all the products remained at the surface? Given that the technique can only provide information on the partitioning of products away from the surface, how can the authors be sure that multiple generations of oxida-

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tion are not occurring prior to material desorbing from the interface?

8) The modelling is performed in such a way that it is not clear if there is any predictive power to the results. For example, the model is fit to the initial decay, and then floated for the remaining time, and in most cases this free-floating region does not do a good job as describing the data. Is this because additional processes are occurring that are not factored into the model? Can the parameters obtained be used to accurately predict the chemistry at different film compressions, oxidant concentration etc.?

9) In the model, partitioning away from the surface (either into the gas phase or bulk aqueous solution) is rapid. Is there any consequence in the modelling for partitioning to one or the other? In these experiments, would the same results be obtained if the products were simply broken down into surface-present and surface-absent? How are partially surface active molecules accounted for in the present analysis?

10) The data for stearic acid is not convincing – while it clearly shows less reactivity, the magnitude of the decay is very small. I would suggest this be removed or moved to the SI to allow for the additional material in the main text to address the previous points in this review.

Minor points:

- 1) A figure in the main text showing the structure of the molecules would make comparisons of the datasets easier for a reader.
- 2) The reference to Section 4 of the SI containing examples of raw data is wrong – there is no raw data presented in the SI.
- 3) Consistency of units (some mixing of [m] and [cm] between text and figures when reporting surface excess).
- 4) Define acronyms consistently, even if they are well known in your field (e.g. FIGARO, PRA)

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5) Define the term “surface excess” – it is unclear in the derivation if this is actually a surface concentration, as equation 2 seems to indicate. If I am correct in my understanding of the difference, for very insoluble species surface concentration and surface excess are approximately equal, but please clarify this.

6) The first paragraph of the “Discussion” would be more appropriate in either the Introduction or the Conclusions.

7) Slightly excessive ‘keywording’

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