

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 #1

Received and published: 4 September 2020

This is the review of the manuscript entitled “Ozonolysis of fatty acid monolayers at the air–water interface: organic films may persist at the surface of atmospheric aerosols.” by Woden et al. This study examines the residual surface film after ozonolysis of an oleic acid monolayer residing on either a water subphase or an aqueous NaCl solution at room temperature and close to the melting point of ice. To characterize the residual film after O₃ exposure, neutron reflectometry and infrared reflection absorption spectroscopy (IRRAS) are applied. It is observed that for colder temperatures a residual film remains, proposed to consist of nonanoic acid and a mixture of azelaic and 9-oxononanoic acids. Furthermore, the second order reaction rate coefficients of O₃ reacting with oleic acid on water and aqueous NaCl solution as subphase were

C1

determined for the two investigated temperatures.

Systematic oxidation studies of organic (surface-active) species at the aqueous-air interface are scarce despite the community’s recognition of its importance to understand the role of aerosol and droplets in various atmospheric processes. This study nicely contributes to the limited data out there. The topic fits well in the Journal Atmospheric Chemistry and Physics. The manuscript is overall well written. One could argue that it could be shorten in some places or that it feels a bit wordy. However, the reader can easily follow the thoughts of the authors. This is more a writing style question and not so much a negative comment. As far as I can assess, the experiments and procedures of these difficult experiments are sound, and the authors do not overinterpret the data; they mention caveats or clearly point out propositions/suggestions. I do not have major criticism, mostly minor revision dealing with experimental conditions, etc. as given below.

The authors mention “near freezing temperatures”. In atmospheric sciences, water droplets freeze at around -37 C and aqueous solutions droplets at even lower temperatures. Thus, I would advise to talk about “near the ice melting” point or temperature, which is 0 C. The aqueous NaCl solution will experience a slight ice melting point depression (see phase diagram and previous studies by the Koop group: [Koop et al., 2000a; Koop et al., 2000b]).

I was surprised that the abstract did not mention at all the use of those state-of-the-art analytical techniques/methods. This could be added.

Line 33: I would add the review by [Rudich, 2003].

Line 47: It turns out that organic monolayers can act as efficient ice-nucleating particles. This could be added as another important role. See discussion in [Knopf et al., 2018] and [Cantrell and Robinson, 2006; Knopf and Forrester, 2011; Zobrist et al., 2007].

C2

Line 49-50: I believe it would be fair to mention the work by Thornton, Abbatt, and Bertram groups: [Cosman et al., 2008; Knopf et al., 2007; McNeill et al., 2006; Thornton and Abbatt, 2005].

Line 86: Methods section. I feel the main text should mention how the monolayers have been characterized. This is essential information and only described in supplement. Also, what were the “ambient” gas-phase conditions during monolayer characterizations and neutron reflectometry and IRRAS measurements? E.g., could water vapor condense onto the monolayer and change the interpretation of the residual film (especially at lower temperatures). Would evaporation of water vapor impact the measurements? I doubt it, but it would be beneficial to have this information to make sure the monolayer was in a similar state among all applied instrumentation. On line 380 there is some indication of this information.

Line 223: “Wider Atmospheric Implications” sounds awkward. My suggestion is to just keep it as “Atmospheric Implications”. Also, line 466.

Line 272 and at lower places in text (discussion of residual film and temperature dependency): The issue of volatility, or more precise, the vapor pressure of the ozonolysis reaction products will depend exponentially on temperature. Going from 20 C to 0 C, depending on the enthalpy of vaporization, this could result in a strong decrease in the vapor pressure and thus lead to accumulation of the species at the interface? I suggest giving the vapor pressure of the reaction products for investigated temperature ranges.

Line 322: I would rephrase to “. . . monolayer is likely not composed of nonanoic acid, . . .”.

Line 434: Instead of “ca” maybe “about”.

Line 440: For kinetic measurements (since it is referred to rate coefficients) there are likely other equally good approaches. I would omit this side sentence.

Supplement:

C3

Line 15-20: I would not mention CaCl₂ at all, since no data is shown and mentioned in main text.

Line 19: “ice melting point”.

Line 21: How many pi-A isotherms were conducted? Uncertainty? Did you measure surface pressure of pure surfaces, i.e. water and aqueous NaCl (see, e.g., Knopf and Forrester, 2011) to check for cleanliness? Was the Langmuir trough temperature controlled and enclosed to avoid laboratory contamination?

Line 39-41: The higher surface pressure may be explained by the addition of NaCl to water which increases the surface pressure, in absence of a monolayer. See, e.g., Knopf and Forrester (2011).

Figure S14: Maybe write out in the figure caption the y-axis parameter, i.e. the meaning of $\rho \cdot \tau$.

References:

Cantrell, W., and C. Robinson (2006), Heterogeneous freezing of ammonium sulfate and sodium chloride solutions by long chain alcohols, *Geophys. Res. Lett.*, 33(7), L07802, doi:L0780210.1029/2005gl024945.

Cosman, L. M., D. A. Knopf, and A. K. Bertram (2008), N₂O₅ reactive uptake on aqueous sulfuric acid solutions coated with branched and straight-chain insoluble organic surfactants, *J. Phys. Chem. A*, 112(11), 2386-2396, doi:10.1021/jp710685r.

Knopf, D. A., P. A. Alpert, and B. Wang (2018), The Role of Organic Aerosol in Atmospheric Ice Nucleation: A Review, *ACS Earth Space Chem.*, 2(3), 168–202, doi:10.1021/acsearthspacechem.7b00120.

Knopf, D. A., L. M. Cosman, P. Mousavi, S. Mokamati, and A. K. Bertram (2007), A novel flow reactor for studying reactions on liquid surfaces coated by organic monolayers: Methods, validation, and initial results, *J. Phys. Chem. A*, 111(43), 11021-11032,

C4

doi:Doi 10.1021/Jp075724c.

Knopf, D. A., and S. M. Forrester (2011), Freezing of Water and Aqueous NaCl Droplets Coated by Organic Monolayers as a Function of Surfactant Properties and Water Activity, *J. Phys. Chem. A*, 115(22), 5579-5591.

Koop, T., A. Kapilashrami, L. T. Molina, and M. J. Molina (2000a), Phase transitions of sea-salt/water mixtures at low temperatures: Implications for ozone chemistry in the polar marine boundary layer, *J. Geophys. Res.*, 105(D21), 26393-26402.

Koop, T., B. P. Luo, A. Tsias, and T. Peter (2000b), Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, *Nature*, 406(6796), 611-614, doi:10.1038/35020537

McNeill, V. F., J. Patterson, G. M. Wolfe, and J. A. Thornton (2006), The effect of varying levels of surfactant on the reactive uptake of N₂O₅ to aqueous aerosol, *Atmos. Chem. Phys.*, 6, 1635-1644, doi:10.5194/acp-6-1635-2006.

Rudich, Y. (2003), Laboratory perspectives on the chemical transformations of organic matter in atmospheric particles, *Chem. Rev.*, 103(12), 5097-5124.

Thornton, J. A., and J. P. D. Abbatt (2005), N₂O₅ reaction on submicron sea salt aerosol: Kinetics, products, and the effect of surface active organics, *J. Phys. Chem. A*, 109(44), 10004-10012, doi:10.1021/jp054183t.

Zobrist, B., T. Koop, B. P. Luo, C. Marcolli, and T. Peter (2007), Heterogeneous ice nucleation rate coefficient of water droplets coated by a nonadecanol monolayer, *J. Phys. Chem. C*, 111(5), 2149-2155, doi:Doi 10.1021/Jp066080w.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2020-717>, 2020.