Authors' Response to Anonymous Referee #1

We are very grateful for the thorough review of our manuscript by referee #1 and the referee's recognition that *"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"*, that our *"study nicely contributes to the limited data out there"*, that the *"topic fits well in the Journal Atmospheric Chemistry and Physics"* and that the *"manuscript is overall well written."*

Below, we respond line-by-line to the referee's specific comments:

- Comment: *"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."*
  Response: we note that several referees commented that the paper could be streamlined; we did carefully re-assess the writing style and volume of text/discussion; we have cut the text a little, but not substantially given completely changing the writing style would be a major effort with little gain and also was not requested by any of the referees; cutting more text would in our view endanger losing the more subtle points of the discussion. The referee clearly states that the reader can easily follow the thoughts of the authors, so that substantial changes seem unnecessary.

- 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."*
  Response: we are grateful for recognition by the referee that method and interpretation are sound and are happy to address the specific suggestions made by the referee.

- Comment: *"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."*
  Response: we are grateful for emphasizing this point: we have changed the wording throughout from "near-freezing" to "near-zero" temperatures ("near the ice melting temperatures" seemed too long to add in each sentences and we are confident that "near-zero" together with the added text will clarify the meaning) and included the valid points mentioned above together with references to the highly relevant work by Koop et al.
  New text: "To this end, we investigated the behaviour at ca. 0 ℃ i.e. near the ice melting temperature (referred to as "near-zero" temperatures in this paper), but it should be noted that aqueous NaCl solutions will experience a slight ice melting point depression (see phase diagram and previous studies, in particular Koop et al., 2000a and Koop et al., 2000b) and that water droplets in the atmosphere will freeze at significantly lower temperatures."

- Comment: *"Line 33: I would add the review by [Rudich, 2003]."*
  Response: we thank the referee and added this relevant reference.

- Comment: *“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].”*
  Response: we are grateful for this suggestion which adds another important aspect; we included these comments and the associated references.
  New text:” Organic monolayers can also act as efficient ice-nucleating particles (see Knopf et al., 2018; Knopf and Forrester, 2011; Zobrist et al., 2007; Cantrell and Robinson, 2006).”

- Comment: *”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].”*
  Response: many thanks for pointing this out: we have added these references that are indeed relevant.

- Comment: *“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).”*
  Response: given we are asked elsewhere to shorten the manuscript, we have kept the details of characterisation in the supplement; we have added a statement clarifying that we continuously flowed dry oxygen at 1.2 L/min though the reaction chamber and at no point did we observe any condensation within the reaction chamber or windows (the liquid was the coldest point).
  New text: “A dry oxygen flow of 1.2 L/min was continuously present, providing a low (< 10 %) R.H. Thanks to this low R.H. we did not observe any condensation within the reaction chamber or windows throughout the experiments.”

- Comment: *“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.”*
  Response: the water level was monitored via a laser and its height in the beam adjusted when necessary. We have added a paragraph in Section 2.1.
  New text:” The height of the air–liquid interface was aligned with respect to the neutron beam using a “Keyence” laser displacement sensor (model no. LK-G402), which was coupled into the sample chamber via a quartz window to allow automated height adjustment during the measurements.”

- Comment: *“Line 223: “Wider Atmospheric Implications” sounds awkward. My suggestion is to just keep it as “Atmospheric Implications”.”*
  Response: we have removed “Wider” from the text.

- Comment: *“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?”*

Response: yes, this is what we are saying. We added further detail in response to comments from this and other referees on this discussion (incl. further details on vapour pressures).

- Comment: *"I suggest giving the vapor pressure of the reaction products for investigated temperature ranges."*
  Response: we have added the estimated vapour pressures of the potential products in Section 3.6.
  New text: "nonanoic acid (estimated vapour pressure at 25 °C: 0.0 ± 0.5 mmHg; all estimated vapour pressures are from ChemSpider), nonanal (estimated vapour pressure at 25 °C: 0.5 ± 0.4 mmHg), azelaic acid (estimated vapour pressure at 25 °C: 0.0 ± 1.8 mmHg) and 9-oxononanoic acid (estimated vapour pressure at 25 °C: 0.0 ± 1.4 mmHg)."

- Comment: *"Line 322: I would rephrase to ". . .monolayer is likely not composed of nonanoic acid,. . .".*
  Response: the suggested wording is not quite consistent with our findings, but we have amended the sentence for clarity to "Based on our analysis, the product monolayer cannot be predominantly composed of nonanoic acid [...]"

- Comment: *"Line 434: Instead of "ca" maybe "about"."*
  Response: we have amended the text.

- Comment: *"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."*
  Response: we have deleted the sentence.

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

- Comment: *"Line 19: "ice melting point".* **Response: text amended.**

- Comment: *"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 –"*
  Response: the absolute value for the surface tension was not always determined; surface cleanliness was assessed by repeated compression decompression cycles; the surface was cleaned until no change in pressure (> 0.5 mN/m) was observed upon full compression.

- Comment: *"Was the Langmuir trough temperature controlled and enclosed to avoid laboratory contamination?"*
  Response: at least three consistent runs were recorded, but only one is presented; the trough was temperature controlled (continuously measured) and enclosed; we were always in the liquid-expanded phase on beam.

- Comment: *"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)."*
  Response: we have added a sentence referring to the paper by Knopf and Forrester.

New text:" These results are consistent with earlier findings by Knopf and Forrester (2011)."

- Comment: *"Figure S14: Maybe write out in the figure caption the y-axis parameter, i.e. the meaning of rho*tau."*
  Response: the figure caption was amended.
  New text:"ρτ is the product of neutron scattering length density and layer thickness is it proportional to the surface excess $\Gamma = \frac{\tau\rho}{b}$, where *b* is the scattering length of the molecule (*d*$_{34}$-OA)."

References: **[all are now included in the revised manuscript]**

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), 11021-11032doi: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

Authors' Response to Anonymous Referee #2

We are grateful for the thorough review of our manuscript by referee #2 and the referee's recognition that 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."*

Below, we respond line-by-line to the referee's specific comments:

- Comment: *"The paper is relatively clear but I reinforce the comments from the previous reviewer* [referee #1] *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."*
  Response: we agree that the key conclusions could be described in a more focussed way and we have made some changes to clarify the key message, but we don't believe that we can remove a substantial volume of the discussion without "any loss of content"; referees #1 and #2 both agree that the paper is clear as written, so that we did not remove 1/3 of the text as suggested by referee #2; we also included 14 new references in response to other referees, so that the overall length of the manuscript could not be shortened significantly.

- Comment: *"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."*
  Response: the experimental apparatus is described in full detail incl. images and a schematic in the associated method paper in *RSC Advances* (Skoda et al., 2017) and we refer to this paper repeatedly in our manuscript. Given referees ask us to reduce the text (this particular referee asks for a reduction by 1/3) we do not think we should repeat what is discussed and depicted in the method paper, but we have added a little more detail in the method section (section 2.1 in particular). The neutron reflectivity experiments were done within three days, during which a constant O_2 flow at 1.2 L/min was passing through the chamber. After deposition of each monolayer, the O_2 flow continued for a few minutes, after which the ozoniser was set to the desired value and ozone was generated. This is clarified in the revised manuscript.

- Comment: *"What is the chamber made of?"*
  Response: the chamber is made of aluminium (as detailed in the method paper we cite). We have added this information in a new paragraph in section 2.1.

- Comment: *"Where is the ozone measured, i.e. before or after the surface?"*
  Response: ozone concentrations are calibrated off-line before and after the beam-time experiments; ozone concentrations cannot be measured during the beam-time experiment due to space-, time- and instrument-limitations; we generally calibrate the concentration entering the reaction chamber, but have performed tests at the chamber exhaust and confirmed consistent concentrations. We have added a paragraph to Section 2.1 to clarify this.

- Comment: *"Could changes of ozone mixing ratio be used to monitor the reaction?"*
  Response: the reactive organic molecules are only present in a single-molecule thin film (monolayer) and the gas-phase oxidant is added in large

excess, so that there is intentionally no significant loss of ozone during the experiment; if we would choose to run the experiment with a lower ozone concentration we would need to be able to reliably monitor these low concentrations continuously before and after the reaction chamber which would require a fundamentally different experimental setup and a highly sensitive online (and mobile) O_3 detection system.
A new sentence in Section 2.3 clarifies our experimental approach: "Mixing ratios of ozone (in O_2) in the chamber were in the range 126 – 2010 ppb, so that we were working in large excess of O_3 compared to the organic monolayer and $[O_3]$ remained approximately constant during the reaction."

- Comment: *"What was the surface area of the substrates?"*
  Response: the trough area was 238 mm × 70 mm; this is stated in the associated method paper (Skoda et al. 2017). We have added this information in the new paragraph in section 2.1.

- Comment: *"How was oleic acid added to it?"*
  Response: monolayers were spread using 20–40 µL of the spreading solutions in chloroform, leaving a monolayer of the dissolved species after evaporation of the solvent; this is stated in the associated method paper (Skoda et al. 2017) and we have also added this information in the new paragraph in section 2.1.

- Comment: *"How was ozone generated?"*
  Response: O_3 was then generated continuously by exposing the O_2 flow to UV light using a commercial pen-ray lamp based ozoniser; this is explained in the method paper (Skoda et al. 2017) and we have added brief descriptions of the ozone generation procedure in sections 2.1 and 2.3.

- Comment: *"Was there NOx present?"*
  Response: No, not in this study- this paper is on ozonolysis reactions (our earlier paper Sebastiani et al., Atmos Chem Phys, 2018 investigated monolayer oxidation by nitrate radicals).

- Comment: *"Is the experiment done in air or nitrogen?"*
  Response: the experiments are carried out in O_2 only (since O_3 was generated by exposing the gas stream to UV light, we chose O_2 and not air for cleaner O_3 generation and avoiding unwanted by-products). We now more clearly state that the gas-phase is O_2 (e.g. new paragraph in section 2.1) to avoid any confusion.

- Comment: *"Was the air preconditioned to 100% RH or is the substrate evaporating all the time?"*
  Response: The reaction chamber received a constant flow of dry O_2 (R.H. in chamber < 10 %); evaporation was possible and was a concern when designing the experiment- we thus continuously monitored the liquid height throughout each experimental run: the height of the air–liquid interface was aligned with respect to the neutron beam using a "Keyence" laser displacement sensor (model no. LK-G402), which was coupled into the sample chamber via a quartz window to allow automated height adjustment during the measurements, but very little height adjustment was necessary (always less than 0.15 mm for a water height of ca. 5 mm in the trough over the duration of a 2-h run). This has been clarified and detailed in the new paragraph in section 2.1.

- Comment: *"Does substantial evaporation occur over the timescale of the experiment?"*
  Response: no - as demonstrated by an often nearly constant liquid level over the duration of the experiments.

- Comment: *"Is the oleic acid a sub-monolayer coverage?"*
  Response: we start with a complete monolayer (at ~ 35 mN/m) and then during oxidation oleic acid molecules are continuously being removed from the surface.

- Comment: *"What is the coverage?"*
  Response: the area per molecule can be calculated from rho*tau as:
  APM = ∑b/(rho*tau).
  Most of our initial monolayers had a rho*tau = 10 cm^{-1}. This corresponds to an area per molecule of 35.8 $Å^2$, which in turn corresponds to about 2.8×10^{14} molecule per cm^2.

- Comment: *"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."*
  Response: we thank the referee for pointing this out - having made the necessary amendments detailed above and in response to the other referees, we believe the readability had been greatly improved. This together with consultation of the method paper (Skoda et al., 2017) should allow to reproduce the measurements (ILL/ISIS beamtime would be needed for neutron reflectrometry experiments, but both facilities have beamlines set up for these experiments).

- Comment: *"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?"*
  Response: we are grateful for the referee pointing out the uncertainties associated with the fate of the Criegee intermediates; this is indeed an important point and we added a comment in the discussion section together with the two references mentioned. However, we are not aware of studies of Criegee intermediates directly applicable to our system of study: while we are happy to reference the papers identified by the referee, we note that the PCCP paper investigates pinonic acid which is quite a different molecule compared to oleic acid given its ring structure, lack of a C=C double bond and polar "tail" group; and the Zhou et al. paper studied a multi-component system including perfluoroalkyl carboxylic acids, so that we do not believe that the conclusions drawn from these papers give direct insight into the behaviour of our floating oleic acid monolayers on water during ozonolysis. For our floating monolayer, we don't think that secondary reactions are very likely given the geometry and relatively low concentration of oleic acid compared to ozone. These monolayer

experiments with neutron reflectometry are challenging, so there is no straight forward avenue to include detection of Criegee intermediates within beamline experiments given time and space constraints; we did not intentionally vary monolayer coverage here (max. variation of coverage was no more than 20% with no measurable effect) and there would not be very much leeway to reduce coverage without getting quickly close to the detection limit. Nevertheless, we included the referee's suggestion to motivate future studies.
New text: "It should be noted that recent work has reported that Criegee intermediates not only re-arrange to form carboxylic acids, but may also react with species such as carboxylic acids leading to formation of hydroperoxide esters (see e.g. work at the air-water interface by Enami & Colussi, 2017 for reactions of cis-pinonic acid with Criegee intermediates produced from ozonolysis of sesquiterpenes and by Zhou et al., 2019 on reactions of condensed-phase Criegee intermediates with carboxylic acids and perfluoroalkyl carboxylic acids). To our knowledge there are no studies on oleic acid reacting with Criegee intermediates, but it is clearly possible that the simple four products presented here are not the only products given the potential for secondary chemistry. For our specific approach of studying a floating monolayer on water, secondary reactions seem comparably unlikely given the geometry and relatively low concentration of oleic acid compared to ozone in the conditions applied. Future studies as a function of oleic acid surface coverage could potentially disentangle this chemistry to some extent and potentially provide evidence for Criegee intermediates reacting with oleic acid."
New references:
Enami, S. & Colussi, A. J., Efficient scavenging of Criegee intermediates on water by surface-active cis-pinonic acid, Phys Chem Chem Phys, 19, 17044, 2017;
Zhou, S., Joudan, S., Forbes, M. W., Zhou, Z. and Abbatt, J. P. D., Reaction of Condensed-Phase Criegee Intermediates with Carboxylic Acids and Perfluoroalkyl Carboxylic Acids, Environ Sci Technol Lett, 6, 4, 243–250, 2019.

- Comment: *"Is there any evidence that the nature of the film changes as the amount of oleic acid on the film decreases?"*
  Response: we are not quite sure what is meant by "nature of film". The monolayer will move along its phase diagram (see Fig. S2 for π-A isotherm of oleic acid monolayer) and is in the liquid expanded phase before and during ozonolysis.

- Comment: *"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?"*
  Response: we cannot estimate the volatility of the compounds directly from our measurements, but we can give an upper bound for the temperature (~ 10 ℃) up to which they remain on the surface.

- Comment: *"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?"*

Response: our experimental set-up is striving to simulate realistic atmospheric conditions with regard to humidity, ozone concentration, pressure and temperature (low temperature conditions of < 10 ℃ occur in the atmosphere more often than 20 ℃). At the same time, we require a carefully controlled environment (constant gas flow, pressure etc.) in order to be able to extract accurate and reproducible information. We thus believe that our results are indeed atmospherically relevant with the caveat that atmospheric compositions of organic materials will be much more complex and we aim to get closer to multi-component atmospheric behaviour in follow-on studies building on this work.

- Comment: *"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?"*
  Response: the residual films are entirely stable on the timescales accessible to us (several hours). We could not follow reactions for longer due to expensive/short beamtime at the large-scale facilities. See also next response (we maintained low partial pressures during the experiments thanks to the flow-through approach, so that we have no reason to believe that lifetimes would be shorter in the atmosphere).

- Comment: *"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?"*
  Response: no – the gas phase is being exchanged at a flow rate of 1.2 L/min, so that we have low partial pressures and the residual films should thus also be stable in an effectively open atmospheric system.

- Comment: *"5. The lack of temperature dependence in the ozone – oleic acid system has previously been shown by Thornberry and Abbatt, PCCP, 2003."*
  Response: we have added a sentence on page 3 commenting on Thornberry and Abbatt's paper, although this was a study on bulk oleic acid (a 0.6 mm thick film), rather than a study of a floating monolayer on water.

- Comment: *"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."*
  Response: we thank the referee for the positive and helpful comments. We have added further explanations to clarify the atmospheric implications.

Authors' Response to Anonymous Referee #3

We are very grateful for the thorough review of our manuscript by referee #3 and the referee's recognition that our *"results provide additional insight."*

Below, we respond line-by-line to the referee's specific comments:

- Comment: "the writing could be more succinct. Similar to the other referees, I suggest reducing the length significantly."
  Response: we have made some changes to clarify the key message, but we don't believe that we can remove a substantial volume of the discussion without any loss of content; referees #1 and #2 both agree that the paper is clear as written; we also included 14 new references in response to other referees, so that the overall length of the manuscript could not be shortened significantly.

- Comment: *"In addition, more discussion on why the films persist in some cases and not others is needed. This fundamental insight is needed to extrapolate the results to the atmosphere. Once, the authors address these results adequately, I would support publishing in Atmospheric Chemistry and Physics."*
  Response: we have added further discussion (incl. 14 additional references) and added specifically a new figure S5(b) to illustrate more clearly that the residual films persist. We have also clarified throughout how the results relate to processes in the atmosphere and atmospheric conditions.

Major comments:

- Comment: *"More discussion on why a surface film was not observed at room temperature but was observed at near-freezing temperatures in the current study is needed. Is the difference due to a difference in vapor pressures or a difference in solubility."*
  Response: we have discussed vapour pressures in response to referee #1 and added estimated vapour pressures for the key products to the manuscript. There are limited data on the temperature dependence of the solubilities of these suspected products, but we found that for azaleic acid the solubility is reduced to 1.0 g/L at 1 °C from 2.4 g/L at 20 °C (O'Neil, M.J. (ed.). The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals. Whitehouse Station, NJ: Merck and Co., Inc., 2006., p. 153). We have added this useful information when discussing the stability of the residue in the discussion section.
  New text: "While there are limited data available on the temperature dependence of the solubilities of these three products, the solubility of azaleic acid has been reported to reduce to 1.0 g/L at 1 °C from 2.4 g/L at 20 °C (O'Neil, 2006) which suggests that azaleic acid may be lost to the subphase at room temperature while being retained at the air–water interface at near-zero temperatures."

- Comment: *"More discussion is needed to understand and rationalize the difference between the results for water at 3.1 degrees C, and NaCl solutions at 3.1 degrees C. A residual film was not reliably measured for NaCl solutions, but it was observed for water at 3.1 degrees C. Can this be explained by differences in solubility? How can the authors justify these results? This insight is needed to extrapolate the results to the atmosphere."*

Response: upon lowering the temperature further by 5 ℃ (to -2 ± 1 °C), a clear residue is also found for the NaCl subphase (see Fig. S5; the new zoomed in Fig. S5(b) specifically illustrates the residue), so we believe that the temperature at which the residue is stable may be slightly lower for salt subphases, but the general observation is consistent with a stable residue in low-temperature atmospheric conditions.

- Comment: *"Page 5: lines 152-155. Some discussion is needed on why a residual film was not observed at room temperature in the current study but was observed in the study King et al. 2009. Did King et al. use different water volumes, different packing densities, different observation times? Can any of these variables explain the difference? Was King et al. more sensitive to material at the surface than in the current study?"*
  Response: we are confident of our results reported here; an upcoming publication by King et al. in Phys Chem Chem Phys on the oleic acid - ozone system will explain the findings in King et al. (2009) and reconcile the results in terms of material retained at the surface; King et al. (2009) was not more sensitive to material at the surface than the current study.

- Comment: *"Page 12, lines 350-353: The authors state that they have demonstrated that a residual film remains at the interface after ozonolysis at -2 degrees C for a NaCl aqueous solution. However, from Fig. 6, this doesn't look like the case. Also, considering the noise in Fig. 2, I am not completely convinced that the residual film reached a stable value at 4*10ˆ3 seconds for a NaCl aqueous solution. If the authors waited until 6*10ˆ3 seconds, would a film still remain on the NaCl subphase at -2 degrees C?"*
  Response: we are confident that the residual film is clearly measureable above the experimental uncertainties in our set-up. For clarity, we have added a new Fig. S5(b) that zooms into figure S5(a) and visually demonstrates that inert material is retained that is then lost upon heating; in the process we have identified a typo in the supplement: the captions for figures S7,8 and 9 have been corrected to read "d_{18}-OA".

- Comment: *"The experiments in the current study occurred on the timescale of 1 hour. Atmospheric time scales can be much longer. What would happen if you waited longer in your experiments?"*
  Response: we could not follow reactions longer due to expensive/limited beamtime at large-scale facilities and thus cannot be sure what would happen in days, but based on the max. 2-h experiments we speculate that the residual film would remain to some extent at the very least.

- Comment: *"Also, the presence of a residual film may depend on the surface to volume ratio of a droplet. How does the surface to volume ratio in your experiments compare to the atmosphere?"*
  Response: the surface to volume ratio of our experimental set-up is not comparable to that of a micron sized droplet. In a droplet, the surface to volume ratio is much larger and thus any potentially solvated molecules will be present at much higher concentrations, thus favouring an increased surface excess. However, since we assume that oxidation products are mostly going into the gas phase, the surface to volume ratio should not play a role. The curvature however could play a role e.g. by changing the phase of the monolayer; but even for micron sized droplets, the curvature should not induce much change in the phase of the fatty acid monolayer.

- Comment: *“Perhaps the presence of a residual film may depend on the vapor pressure of the reaction products and the amount of material in the gas phase. How do your experimental conditions compare to the atmosphere, in this respect? A fundamental understanding is needed to extrapolate the laboratory results to the atmosphere.”*
  Response: there are only negligible amounts of reaction products in the gas phase since the reaction chamber is under constant flow of O_2 at 1.2 L/min and the conditions are realistic for the lower troposphere; we have clarified this in section 2.1.
  New text: “A dry oxygen flow of 1.2 L/min was continuously present, providing a low (< 10 %) R.H. and avoiding any build-up of gas-phase products that would not be consistent with atmospheric conditions.”

Minor comments:

- Comment: *“Page 3, lines 80-86. The secondary analysis technique, IRRAS, is mentioned, but the primary analysis technique in the study is not mentioned.”*
  Response: the primary analysis method is neutron reflectometry; we have added a paragraph with further detail in section 2.1.

- Comment: *“If the authors mention the secondary analysis technique here, they should also mention the primary analysis technique. Section 2.1. Is the technique sensitive to the tilt angle of the surfactant at the interface, with respect to the surface normal?”*
  Response: neutron reflectometry is in principle able to determine the thickness of layers (and thus for a known molecule length, a tilt angle can be inferred). In our case however, the thickness information is highly correlated with the monolayer density or volume fraction. In addition, since the oleic acid molecules are not linear, a high level of disorder is to be expected in the monolayer, such that it would be impossible to quantify a global tilt angle in any case.

- Comment: *“Page 6: line 176, and elsewhere in the manuscript. The authors imply that a temperature of 3 degrees C is more atmospherically relevant than 21 degrees C. They are both atmospherically relevant temperatures. At the surface and over the tropics, 21 degrees C is more common. I would remove “more atmospherically relevant” from the discussion when comparing the two temperatures. If the authors want to focus on the free troposphere, then maybe “more atmospherically relevant” is appropriate.”*
  Response: we do believe that our findings are still relevant for most of the atmosphere (though perhaps more applicable to temperate and polar regions and with the exception of the boundary layer in the tropics). In addition, oleic acid has an atmospheric lifetime of days, so typical aerosol particles will experience lower temperatures during their lifecycles.
  New text added: “Near-zero temperatures are more frequently encountered in the atmosphere than room-temperature conditions used in other studies especially in temperate and polar regions as well as in the free troposphere possibly with the exception of the boundary layer in the tropics.”

- Comment: *“Page 7, line 216. Here and elsewhere, the authors refer to a film impervious to further ozone. This implies that ozone cannot pass through the film, which was not shown in the current study. Please change “impervious” to “unreactive” or something similar.”*
  Response: we have changed the wording.

Authors' Response to Anonymous Referee #4

We are grateful for the review of our manuscript by referee #4 and the referee's recognition that our *"results could inspire a lot of future researches such as exploring atmospheric oxidation products and kinetics of cooking aerosols using chamber/flow tube under indoor/outdoor environment"* and that this *"paper has a clear logical structure and is easy to follow. The methods and assumptions are valid and clearly outlined, and the results are well discussed."*

Below, we respond line-by-line to the referee's specific comments:

- Comment: *"the paper is too long and seems a little wordy. I would recommend shorten it."*
  Response: we have made some changes to clarify the key message, but we don't believe that we can remove a substantial volume of the discussion without any loss of useful content; referees #1 and #2 both agree that the paper is clear as written and we also included 14 new references in response to other referees, so that the overall length of the manuscript could not be shortened significantly.

- Comment: *"I have a few suggestions on the following areas: 1) Simulated atmospheric environment: the temperature (<10 ◦C) in this study is not highly atmospheric relevant if considering summer seasons (20~40 ◦C). People like to grill in the summer, generating a lot of aerosols coated with fatty acids. I think the condition in this study might be more relevant to winter seasons. Also, this study doesn't include any relative humidity (RH) information. RH can greatly affect aqueous phase chemical reactions and is important for describing the reaction environment."*
  Response: we do believe that our findings are still relevant for most of the atmosphere (though perhaps more applicable to temperate and polar regions and with the exception of the boundary layer in the tropics). In addition, oleic acid has an atmospheric lifetime of several days, so that typical aerosol particles will experience lower temperatures. We have included additional information, also about R.H. in section 2.1.

- Comment: *"2) Section 3.4 Atmospheric Aging Simulation: The authors observed that "yet more oleic was added, and a third ozonolysis reaction carried out", and concluded that the product monolayer is impervious to further ozonolysis. There are other factors that might slow down the reaction rate of ozonolysis. For example, the water surface might already be saturated with the products."*
  Response: we are confident that this is not the case - the neutron reflectometry signal intensity allows us to quantify the amount of oleic acid on the surface. A rho*tau value of 10^3 corresponds to a surface pressure of approximately 35 mN/m or a coverage of ~2.8×10^{14} molecules per cm^2. As can be seen from the figures, we can monitor this value very accurately. Given that the rate of decay is consistent with earlier studies (our own included), we can rule out the presence of an additional source/reservoir of oleic acid.

- Comment: *"Even if you add more reactants, the reactions might not happen without removing previous products in the organic layer. I suggest the authors add more evidence to this conclusion."*
  Response: we cannot deconvolute the exact process, but the result remains that a non-oxidisable residue is retained at the surface at low temperatures.

- Comment: *“Grammar or spelling problems: 1) “3.4 Atmospheric Ageing Simulation”, change “ageing” to “aging” “*
  Response: we are adhering to British English spelling throughout and did not identify any spelling problems.

Ozonolysis of fatty acid monolayers at the air–water interface: organic films may persist at the surface of atmospheric aerosols.

Benjamin Woden[1,2], Maximilian W. A. Skoda[2], Adam Milsom[3], Armando Maestro[4], James Tellam[2] and Christian Pfrang[3,5].

[1]Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK.
[2]ISIS Neutron and Muon Source, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Didcot, OX11 0QX, UK.
[3]School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK.
[4]Institut Laue Langevin (ILL), 71 Avenue des Martyrs, Grenoble, 38000, France.
[5]Department of Meteorology, University of Reading, Whiteknights Road, Reading, RG6 6BG, UK.
Correspondence to: Christian Pfrang (c.pfrang@bham.ac.uk)

Abstract. Ozonolysis of fatty acid monolayers was studied to understand the fate of organic-coated aerosols under realistic atmospheric conditions. Specifically, we investigated the effects of temperature and salinity on the degradation of oleic acid at the air–water interface and the persistence of the aged surfactant film at the surface. The presence of a residual film is of atmospheric importance, as surface monolayers affect the physical properties of the droplets and because of the role they play in cloud formation. This occurs via several effects, most notably via surface tension reduction. The interplay between atmospheric aerosol loading and the formation, nature, and persistence of clouds is a key uncertainty in climate modelling. Our data show that a residual surface film, which we suspect to be formed of nonanoic acid and a mixture of azelaic and 9-oxononanoic acids, is retained at the interface after ozonolysis at near-zero temperatures, but not at room temperature. Given the low temperature conditions used here are atmospherically realistic, the persistence of a product film must be considered when assessing the impact of unsaturated fatty acid partitioned to the air–water interface. The presence of stable (non-oxidisable) reaction products also opens the possibility of build-up of inert monolayers during the aerosol life-cycle with potential implications for cloud formation. Furthermore, we measured the kinetic behaviour of these films and found that the reactions are not significantly affected by the shift to a lower temperature with rate coefficients determined to be (2.2 ± 0.4) × 10^{-10} cm^2 s^{-1} at 21 ± 1 °C, and (2.2 ± 0.2) × 10^{-10} cm^2 s^{-1} at 2 ± 1 °C.

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1 Introduction

Organic films are formed at the surfaces of aerosol particles in the atmosphere (Gill et al., 1983; Ellison et al., 1999; Sareen et al., 2013; Noziere et al., 2014; Kroflic et al., 2018; Gerard et al., 2019), and the partitioning of organic components in this manner changes the physical properties of the aerosol particle and its chemical reactivity (Rudich, 2003; Ruehl et al., 2016;

Ovadnevaite et al., 2017). A key review (Donaldson and Vaida, 2006) has brought together various emerging trends in the study of these films and their relevance to atmospheric processes. An important area of interest regarding these films concerns the interactions between atmospheric aerosol particles and clouds. This relationship is complex and difficult to measure or predict (Stevens and Feingold, 2009), and resolving the role played by organic monolayers at the surface of aerosol particles is part of solving this puzzle. The organic species that are contained in these surface films oxidise in the atmosphere and may produce low volatility products that form secondary organic aerosols. If the oxidation of these species is prevented, accelerated, or otherwise modified by the partitioning of the reactant into a surface monolayer, then this will have implications for the contribution of that reactant to aerosol loading. More importantly, the presence of a surface monolayer changes the physical and chemical properties of the aerosol particle itself.

The present study focuses on monolayers at the air–water interface as would be seen on aqueous aerosol droplets, but the concept is broadly transferrable to any aerosol particle with an organic film coating. These monolayers are relevant, as they decrease the surface tension of water (Donaldson and Vaida, 2006; Ambaum, 2010); the surface tension of aqueous droplets plays a key role in the growth and formation of clouds (Ambaum, 2010; Ovadnevaite et al., 2017). Furthermore, the monolayer can act as a barrier to water uptake, retard droplet evaporation, and inhibit the transfer of atmospheric species between the air and water phases (Rideal, 1924; La Mer, 1962, 1964; Gaines, 1966; Garrett, 1971; Ray et al., 1991; Benjamin, 1996; Barnes, 1997; Li et al., 2019). It can also act as a '2D solvent' for normally water-insoluble species that could not partition to a water aerosol or modify the solvation behaviour of soluble species (Tomoaia-Cotisel and Cadenhead, 1991; Cohen Stuart et al., 1996; Mmereki and Donaldson, 2002; Mmereki et al., 2003; Gilman et al., 2004). Organic monolayers can also act as efficient ice-nucleating particles (see Knopf et al., 2018; Knopf and Forrester, 2011; Zobrist et al., 2007; Cantrell and Robinson, 2006).

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This catalogue of effects upon the aerosol particle caused by the presence of an organic monolayer coating shows the importance of establishing the lifetime and ageing of these monolayers in the atmosphere, and this has been the focus of previous research (e.g. Thornton and Abbatt, 2005; Hung et al., 2005; Knopf et al., 2005; McNeill et al., 2006; Voss et al., 2007; Knopf et al., 2007; Cosman et al., 2008; Gross et al., 2009; King et al., 2009; Pfrang et al., 2014; Sebastiani et al., 2018).

Oleic acid has been a monolayer component of particular interest, as it is a major contributor to both anthropogenic organic emissions (it is mostly produced by meat cooking (Shrivastava et al., 2007) and is the dominant component of such emissions (Allan et al., 2010)) and biogenic marine aerosols (Tervahattu et al., 2002; Fu et al., 2013). Its ubiquity in such aerosols has allowed it to serve as a benchmark molecule for more complex mixtures of organic surfactant produced by such anthropogenic activity (Zahardis and Petrucci, 2007). While there are numerous studies of pure oleic acid or high oleic acid content droplets and their oxidation reactions (e.g. King et al., 2004; Voss et al., 2007; Last et al., 2009; Pfrang et al., 2017), work on the oxidation of an oleic acid monolayer at the air–water interface in particular has been comparatively scarce (King et al., 2009; Skoda et al., 2017; Sebastiani et al., 2018).

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Ozone (O_3) and nitrate radicals ($NO_3^{\bullet}$) are important night-time oxidants (e.g. Hung et al., 2005; Gross et al., 2009; Sebastiani et al., 2018; Woden et al., 2018), while O_3 and hydroxyl radicals ($^{\bullet}OH$) are the key day time oxidants (see Chen et al., 2020 for a recent study of heterogenous OH reactions on organic aerosols). Of these three primary atmospheric oxidants O_3 is the only one present during the day and night and the present study is focused on ozonolysis, i.e. oxidation by O_3.

The initial reaction of O_3 with oleic acid is chemically well understood, and is laid out in Scheme 1 (compare King et al., 2009; see also Gallimore et al., 2017). It proceeds via an attack on the carbon–carbon double-bond at the centre of the molecule. The two reaction pathways resulting from the two possible collapses of the molozonide lead to a total of four initial reaction products. These products are nonanoic acid, nonanal, 9-oxononanoic acid, and azelaic acid (Zahardis and Petrucci, 2007). One detailed kinetic study on bulk-like oleic acid (Thornberry and Abbatt, 2003) identifies nonanal as major product with a yield of 0.50 (±0.10) for the oleic acid ozonolysis using a coated-wall tube (0.6 mm thick oleic acid layer). The authors found only a small temperature dependence of the uptake coefficients down to 263 K. The fate of these products after the ozonolysis of an oleic acid *monolayer* however is the subject of debate (Voss et al., 2007; King et al., 2009).

The presence of a product partitioned to the (air–water) interface after reaction is the most important question for atmospheric impact, as a monolayer remaining after ozonolysis may perpetuate the modifications to the properties of an aerosol droplet due to the persistence of the organic character at the air–water interface even after ozonolysis (Ellison et al., 1999; Donaldson and Vaida, 2006).

The aim of this study is to extend the understanding of oleic acid monolayer ozonolysis under atmospherically relevant conditions by investigating the impact of low temperatures and saline subphases. King et al. (2009) investigated a variety of saline subphases, but did not study differences in ozonolysis behaviour between the monolayers spread upon them at room temperature, and to our knowledge no studies have yet investigated the effects of low temperatures (< 10 °C), which are common in the lower troposphere (Grotjahn, 2015), where these reactions occur. To this end, we investigated the behaviour at ca. 0 °C i.e. near the ice melting temperature (referred to as “near-zero” temperatures in this paper), but it should be noted that aqueous NaCl solutions will experience a slight ice melting point depression (see phase diagram and previous studies, in particular Koop et al., 2000a and Koop et al., 2000b) and that water droplets in the atmosphere will freeze at significantly lower temperatures. Near-zero temperatures are more frequently encountered in the atmosphere than room-temperature conditions used in other studies especially in temperate and polar regions as well as in the free troposphere possibly with the exception of the boundary layer in the tropics. Our neutron reflectometry (NR) study also incorporates simultaneous characterisation by infrared reflection absorption spectroscopy (IRRAS) as a secondary analysis technique, using a bespoke reaction/analysis chamber recently developed for this purpose (Skoda et al., 2017).

2 Methodology

This research was performed on the specular neutron reflectometry instruments INTER at the ISIS Neutron and Muon Source and FIGARO at Institut Laue Langevin (ILL) and builds on previous work by this research group on the oxidation of floating monolayers at the air–water interface performed at these facilities (Pfrang et al., 2014; Sebastiani et al., 2015; Skoda et al., 2017; Sebastiani et al., 2018; Woden et al., 2018).

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2.1 Neutron Reflectometry

A review paper (Lu et al., 2000) details how neutron reflectometry can be used to determine the surface concentration of organic films present as a monolayer at the air–water interface. In short, neutron reflectivity depends on the differences between concentrations of atoms with a characteristic neutron scattering length in adjacent thin layers of material. Simplifications of the equations describing this system are possible when studying just one layer (the organic monolayer) at the interface between air (which essentially has a scattering length density (SLD) of zero) and a 'null reflecting' or 'air-contrast matched' subphase (a subphase prepared to have a neutron SLD of zero, matching that of air). Null reflecting matched water was prepared as a solution of D_2O (99.9 % Atom D; Sigma-Aldrich) 8.8 % v/v in 18.2 MΩ H_2O. Null reflecting sodium chloride solution subphase was prepared with 35 g NaCl (< 99 %; Sigma-Aldrich) in 900 mL H_2O and 58 mL D_2O. This preparation compensates for the scattering length of the salt ions with a slightly different H_2O/D_2O ratio.

Details of the experimental setup and procedure can be found in Skoda et al. (2017). In short, a purpose-built aluminium gas flow cell with a volume of approximately 1.5 L was used, which accommodated a PTFE liquid trough with inner dimensions of 238 mm × 70 mm. The sample stage was equipped with passive and active anti-vibration control. The reaction chamber was mounted on the sample stage and interfaced with the gas setup. The PTFE trough was filled with 90 mL of ACMW. Monolayers were spread using 20–40 µL of the spreading solutions in chloroform, leaving a monolayer of the dissolved species after evaporation of the solvent. A dry oxygen flow of 1.2 L/min was continuously present, providing a low (< 10 %) R.H. and avoiding any build-up of gas-phase products that would not be consistent with atmospheric conditions. Thanks to the low R.H., we did not observe any condensation within the reaction chamber or windows throughout the experiments. Data were recorded for a few minutes before O_3 was admitted into the chamber. O_3 was then generated continuously by exposing the O_2 flow to UV light. The height of the air–liquid interface was aligned with respect to the neutron beam using a "Keyence" laser displacement sensor (model no. LK-G402), which was coupled into the sample chamber via a quartz window to allow automated height adjustment during the measurements. Height adjustments over a 2-h experiment were always less than 0.15 mm for a water height of ca. 5 mm in the trough. The reflectivity (fraction of incident neutrons reflected; *R*) varies as a function of the energy and reflection angle of the incident neutrons (expressed as momentum transfer (*Q*)) and the SLD (ρ) and thickness (τ) of the monolayer as expressed in Eq. (1) (based on Lu et al., 2000).

$$\frac{Q^4 R}{16\pi^2} \cong 4\rho^2 sin^2 \frac{Q\tau}{2} \qquad (1)$$

The SLD and layer thickness characteristic of the system can then be inferred from the relationship between reflectivity and momentum transfer as measured by the instrument. The two parameters are fitted over the whole Q-range as a combined ρτ value, which corresponds to a surface concentration of scattering length, from which the surface concentration of oleic acid can be determined as the scattering length of oleic acid is known (b = 315 fm). Reflectivity curves of *R* vs *Q* are collected at 20 s intervals throughout the reaction and fitted using MOTOFIT (Nelson, 2006), to give ρτ values for each timeslice. These fitted ρτ values can be converted into surface concentration (Γ) values for oleic acid (Eq. (2), based on Lu et al., 2000).

$$\Gamma = \frac{\tau\rho}{b} \qquad (2)$$

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In order for the layer to stand out sufficiently from the other phases, a deuterated form, *d*$_{34}$-oleic acid, was used. Spreading onto an aqueous subphase will cause the acidic deuterium to be exchanged with the subphase, so we use the scattering length of oleic acid with 33 deuterium atoms (315 fm) to calculate the surface concentration from ρτ values. For product identification studies, we used custom-synthesised half-deuterated *d*$_{18}$-oleic acid.

2.2 Reaction chamber for simultaneous infrared reflection absorption spectroscopy (IRRAS)

The reactions were carried out in a bespoke chamber developed by this research group. The chamber is designed to provide a controlled and confined environment in which the monolayer can be oxidised by a gas phase oxidant while under analysis by both neutron reflectometry and IRRAS. The integration of IRRAS analysis *in situ* during the neutron reflectometry experiment is non-trivial, and the entire analysis and reaction setup is described in detail in a method paper (Skoda et al., 2017). For this study it had been further developed to allow for cooling of the subphase, in order to access relevant atmospheric temperature conditions. IRRAS integration is primarily intended to facilitate the study of mixed monolayers, in which one component can be deuterated (for neutron reflectometry) and the other left non-deuterated (and thus easily measurable by IRRAS). This work focuses on a film composed solely of oleic acid, so the IRRAS analysis served as an additional semi-quantitative method to follow the oleic acid component, rather than as a method to follow non-deuterated film components (Skoda et al., 2017). During experiments using *d*$_{18}$-oleic acid, IRRAS data were sensitive to the deuterated and non-deuterated halves of the molecule (via the C–D and C–H absorption bands, respectively). The IRRAS equipment was only available at the INTER beamline, given the large and flexible sample environment available at that instrument.

Baseline-corrected integrations under C–D peaks (symmetric and asymmetric stretch) provide a series of peak area against time traces for each reaction, which reflect the presence or absence of CD chains at the surface and traces their evolution throughout the reaction.

While IRRAS can measure deuterated components (the IR absorbance bands are shifted to a lower wavenumber, distinguishing them from the absorbance bands associated with non-deuterated components), the sensitivity in this region is much lower, as these bands are weaker and more affected by the gas-phase atmosphere above the organic film. This meant that the IRRAS measurements could not distinguish the residues left at low temperatures from background noise. Figure S13 in the Electronic Supplement shows an example of IRRAS data from an ozonolysis experiment on INTER.

2.3 Materials

d$_{34}$-oleic acid was used (one batch custom-synthesised by the ISIS Deuteration Facility and one batch purchased from Sigma-Aldrich at 98 % Atom D; 99.9 %); the half-deuterated *d*$_{18}$-oleic acid was produced by the ISIS Deuteration Facility; O_3 was produced for the reaction using a commercial pen-ray ozoniser (UVP Ltd, Cambridge) to ozonise a stream of O_2 (99.999 %; BOC) regulated to a flow of 1.2 L min^{-1} (20 cm^3 s^{-1}) using an electronic mass flow controller to an O_3 concentration of (1.43 ± 0.05) × 10^{13} cm^{-3}; the ozoniser was calibrated offline using UV-Vis absorption at 254 nm and an absorption cross-section value of 1.13 × 10^{-17} cm^{-2} (Daumont et al., 1992). Mixing ratios of ozone (in O_2) in the chamber were in the range 126 – 2010

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ppb, so that we were working in large excess of O_3 compared to the organic monolayer and [O_3] remained approximately constant during the reaction.

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3 Results and Discussion

Prior to the ozonolysis studies we characterised the stability of the oleic acid monolayers at room and reduced temperatures (see Section S1 of the Electronic Supplement with π-A isotherms presented as Figures S1 and S2). After confirming the reactant film's stability, we exposed the monolayers to ozone following the reaction by neutron reflectometry and IRRAS in the conditions described below.

3.1 Pure Water Subphase – Room Temperature

At room temperature, on a pure water subphase, we found that the removal of deuterated material from the surface is consistent with complete oxidation. The remaining reflectivity signal is not distinguishable from zero and cannot be fitted except by using a fixed background. This is consistent with the results of Voss et al. (2007), but not with those of King et al. (2009), where a stable product film was reported.

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Figure 1 shows a time series of fitted ρτ values (proportional to surface concentration) for 120 s time slices of the reaction, with an O_3 concentration of 323 ± 9 ppb introduced at $t = 0$ s. The absence of points after ca. 800 s indicates that the numerical fits fail to converge after this point, demonstrating that the reflectivity is not consistent with an adsorbed surface layer (i.e. not measurably different from the background). Figure S3 in the Electronic Supplement illustrates this as a pair of before/after R vs Q reflectivity curves. The figure also shows data for a salt subphase reaction, which will be discussed below.

This result of no measurable residue was reproducible across 11 different ozonolysis runs carried out across an [O_3] range of 126 ± 15 to 2010 ± 238 ppb as parts of three different beamline experiments at two different neutron facilities (ISIS INTER RB 1810793 and RB 1710483; ILL FIGARO 9-10-1518).

3.2 Salt Water Subphase – Room Temperature

Sea spray aerosol will naturally be salty, and a simple monovalent common salt, sodium chloride (aq; 36 g L^{-1}) was used as a rough model of sea spray for this experiment.

At room temperature, the reaction also proceeded to completion, with no residual deuterated material detectable at the interface. King et al. (2009) found that there was no detectable difference in the nature of the reaction between a room temperature pure water subphase and a room temperature salted subphase (across a wider variety of salts than studied here), and these results support that comparative conclusion (though King et al. actually measured a residual layer in both conditions while the present study has measured no residual layer in either condition; this experiment supports their finding that no *difference* between the reaction in the two conditions is detectable using this method). Figure 1 shows the results in these conditions as a time series of 120 second time slices (a lack of points indicates no convergence in the numerical fit; a pair of before/after *R* vs *Q* reflectivity curves can be found as Figure S4 in the Electronic Supplement).

3.3 Near-Zero Temperature Conditions: Pure Water Subphase

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Experiments were then undertaken to determine if the reaction proceeds in a similar manner at atmospherically more relevant temperatures of 3 ± 1 °C. A clear difference between this reaction and the reaction at room temperature is observable. At the lower temperature, the neutron reflectometry data clearly show a residual signal from deuterated material at the interface after the initial reaction of oleic acid and ozone. On heating the subphase to room temperature, this residue disappears. This is inferred from the fact that, after heating, the reflectivity signal is consistent with that for a null reflecting water surface (i.e. background), meaning that no deuterated material remains at the surface (or so little that it cannot be distinguished from this background condition[1]); the reflectivity data for such a null reflecting air–water interface are included in the electronic supplement (Figure S11).

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The kinetics of the reaction, however, do not seem to differ markedly in the two temperature conditions. A fuller treatment of the kinetics of the reaction (in which we confirm no significant difference in 2nd-order rate coefficients for the two temperature conditions) will follow in Section 3.9.

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Figure 2 shows a time evolution plot for these conditions. It demonstrates that a stable residual layer remaining after ozonolysis for more than one hour can be measured and fitted over 120 s counting periods, and that this is no longer the case after heating to 20 °C. The figure also shows data from a salt subphase reaction, which will be discussed below. Figure 3 draws particular attention to the distinction between the situation after ozonolysis and the situation after heating by showing *R* vs *Q* reflectivity curves before ozonolysis, after ozonolysis and after heating (the analogous plot for the salt water condition is included in the electronic supplement as Figure S5).

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This measurable residue after ozonolysis is reproducible across 18 experiments carried out with a wide $[O_3]$ range from 126 ± 15 ppb to 2010 ± 238 ppb. The lower end of this range is close to mixing ratios of 100 ppb that have been observed in polluted conditions (Warneck, 1999) and thus approaches atmospherically realistic concentrations as far as feasible within the time constraints of beamtime experiments for such a rigorous study.

Twelve of these runs (those obtained at the high-flux instrument FIGARO at ILL; experiment 9-10-1518) were carried out to determine the kinetic behaviour of this reaction, and were therefore performed using a high d*Q*/*Q* fast (5 s per measurement) chopper and slit setup optimised for kinetic measurements of the fast reactions afforded by high $[O_3]$. These runs were used to measure 2nd-order rate constants for the reaction (cf. Section 3.9) rather than to precisely quantify the residual material.

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[1] The exact value of this cut-off point varies depending on measurement conditions and count time, but SLD*thickness values as low as 5×10^2 cm^{-1}, corresponding to ca. 5 % of the oleic acid concentration spread initially, have been reliably measured with this experimental setup.

Therefore, these 12 runs support the qualitative conclusion that a residue remains after ozonolysis, but were not used to quantify this residue.

Four runs (INTER; experiment RB 1810793) were carried out with the precise and reproducible temperature control system and with the neutron reflectometry setup optimised to facilitate precise measurement of a low intensity reflectivity signal (low dQ/Q, low background). These were assumed to be sampling from a Gaussian distribution of residue intensities, and on that basis a mean deuterated residue fraction of 11.1 % of the initial spread material was calculated, with a 95 % confidence interval of ± 1.9 % (absolute).

3.4 Atmospheric Ageing Simulation

In order to provide further assurance that the measured residue was a genuine product monolayer and not, for example, a temperature-dependent fitting artefact, an experiment was performed in which, after ozonolysis of an oleic acid monolayer, more oleic acid was added and another ozonolysis reaction carried out, and then yet more oleic was added, and a third ozonolysis reaction carried out. If the measured residual reflectivity is due to a product monolayer, then this should build up over multiple spreading and ozonolysis cycles. This was indeed observed, adding further weight to the conclusion that the measured residual reflectivity stems from the presence of a product monolayer that is not susceptible to further ozonolysis. Figure 4 shows a time series representing reflectivity from the air–water interface at 120 s time slices throughout this process, and clearly demonstrates the gradual build-up of a product monolayer. As well as illustrating that this is a real product, not a temperature-dependent measurement artefact, this represents a possible process in the real atmosphere, in which reactive species could be repeatedly adsorbed to the surface and engage in reactions which leave small amount of unreactive material behind, gradually building up an unreactive monolayer. The atmospheric implications of this, which are potentially significant, are discussed in Section 4.2.

Figure 5 further illustrates this as a series of R vs Q reflectivity curves for each spreading and ozonolysis (as well as for a final heating step; data for 2nd and 3rd spreading steps are omitted and only fits shown as all three data series heavily overlap), and Figure S6 in the Electronic Supplement focuses in on the build-up of the product monolayer by excluding the spreading R vs Q curves from the plot and zooming in on the post-ozonolysis reflectivity data. In Figure 5, the data points for the spreading of additional material (two series) are removed for clarity (they very closely overlap the initial spreading data), and only the fits are shown.

3.5 Near-Zero Temperature Conditions: Salt Water Subphase

Ozonolysis reaction was also carried out on a simple monovalent sea salt solution model subphase. At the same temperatures where a residue was observed on pure water (3 ± 1°C), a residue was not reproducibly measurable for the salt-water subphase: only one out of five runs carried out with the temperature control setup produced a measurable residue, and it is possible that this residue was not stable, but was still slowly disappearing – see discussion below on the unexpected kinetics of the reaction

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in these conditions. This could be because no residue remains under these conditions, or because whatever residue does remain is close to the detection limit for this technique.

However, at still colder temperatures not accessible on a pure water subphase (-2 ± 1°C), a residue is reliably measurable. Figure 2 shows a time evolution for a reaction in these conditions, and Figure S5 in the Electronic Supplement shows the corresponding *R* vs *Q* plots for spreading, ozonolysis, and heating.

This result was produced in duplicate (INTER experiment RB 1810793). Using the same assumption of sampling from a Gaussian distribution of measured residues as a fraction of initially deposited deuterated material as used in the pure water at 3 ± 1 °C, the mean deuterated residue fraction of 7.3 % was calculated, with a 95 % confidence interval of ± 0.4 5% (absolute). The upper confidence bound of this mean lies below the lower confidence bound of the mean for the pure water at 2 ± 1 °C. This supports the conclusion that a little less product monolayer remains at the interface in the salt water at -2 ± 1 °C condition than in the pure water at 3 ± 1 °C condition.

A basic visual appraisal of the time evolution of this reaction (see Figure 2) also suggests a considerable difference in the kinetics of the reaction compared with those seen at room temperature, and on pure water at low temperatures. Instead of the linear-to-exponential decay (either to no signal, or to a residual signal) seen under other conditions, the reaction appears to follow a linear-to-exponential decay at first, before switching to a much slower roughly linear decay to the final residual monolayer. This shape was reproducible across three runs under these conditions, as well as in five runs with the salt subphase at 3 ± 1°C. One of these five runs in which a residue was detectable may have simply been a slow linear decay that was not allowed to run to completion – as this arresting of exponential decay and replacement with a much slower linear decay was unexpected, it was initially difficult to distinguish from the stable residual monolayer, as seen in pure water at 3 ± 1 °C and after the slow linear decay in salt water at -2 ± 1 °C.

We can currently only speculate about what exactly is causing this deviation from expected stretched exponential decay in the low temperature salt water conditions. The most likely explanation seems to be that some deuterated products are building up on the surface throughout the reaction and then slowly partitioning away from the interface (in a process which goes to completion at 3 ± 1 °C but not at -2 ± 1 °C).

3.6 Product Elucidation With Partially Deuterated Reactants at Near-Zero Temperatures: Pure Water Subphase

In order to understand what the atmospheric impacts of this product monolayer are likely to be, it is important to understand its composition. The ozonolysis of oleic acid (see Scheme 1) produces four initial products: nonanoic acid (estimated vapour pressure at 25 °C: 0.0 ± 0.5 mmHg; all estimated vapour pressures are from ChemSpider), nonanal (estimated vapour pressure at 25 °C: 0.5 ± 0.4 mmHg), azelaic acid (estimated vapour pressure at 25 °C: 0.0 ± 1.8 mmHg) and 9-oxononanoic acid (estimated vapour pressure at 25 °C: 0.0 ± 1.4 mmHg). It should be noted that recent work has reported that Criegee intermediates not only re-arrange to form carboxylic acids, but may also react with species such as carboxylic acids leading to formation of hydroperoxide esters (see e.g. work at the air–water interface by Enami & Colussi (2017) on reactions of cis-pinonic acid with Criegee intermediates produced from the ozonolysis of sesquiterpenes and by Zhou et al. (2019) on reactions

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of condensed-phase Criegee intermediates with carboxylic acids and perfluoroalkyl carboxylic acids). To our knowledge there are no studies on oleic acid reacting with Criegee intermediates, but it is clearly possible that the simple four products presented here are not the only products given the potential for secondary chemistry. For our specific approach of studying a floating monolayer on water, secondary reactions seem comparably unlikely given the geometry and relatively low concentration of oleic acid compared to ozone in the conditions applied. Future studies as a function of oleic acid surface coverage could disentangle this chemistry to some extent and potentially provide evidence for Criegee intermediates reacting with oleic acid.

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Out of the four initial products described in Scheme 1, nonanoic acid is the most obviously amphiphilic product, and thus the prime candidate picked out in the past for possible membership in a post-ozonolysis monolayer (King et al., 2009). Nonanal has been reported as partitioning to the gas phase upon oxidation of methyl oleate monolayers (McNeill et al., 2007). The surfactant activity of azelaic acid is under debate, with Voss *et al.* suggesting no surfactant activity (Voss et al., 2007) and Tuckermann taking the opposite view (Tuckermann, 2007). The room-temperature solubility of azelaic acid (2.4 g L^{-1} (Tuckermann, 2007)) is much higher than that of nonanoic acid (0.28 g L^{-1} (Gilman et al., 2004)), so, in a reaction producing both products, azelaic acid is more likely to partition into the bulk rather than to the interface, although there is no conclusive evidence that it does not partition to the interface. King et al. (2009) suggest that it most likely partitions to the bulk. 9-Oxononanoic acid is not as well studied as the other products, and therefore is the hardest to predict as regards to its partitioning. King et al. (2009) suggest tentatively that it does not partition to the interface.

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From the results discussed so far and knowledge of the volatility, solubility, and amphiphilicity of the candidate species, it is reasonable to dismiss nonanal from consideration due to its measured partition to the gas phase in a very similar reaction, and due to the lack of any obvious significant amphiphilicity in the structure of the molecule. The results discussed so far do not allow discernment between nonanoic acid, azelaic acid and 9-oxononanoic acid, all of which, if present as product monolayers, could produce the observed results.

However, the use of a partially deuterated form of oleic acid allows for some discernment between possibilities. Deuteration of only the tail-side of the double-bond of the oleic acid molecule (shown in teal in Scheme 1) facilitates an ozonolysis reaction in which two of the products (nonanal and nonanoic acid) will be deuterated (and thus detectable via neutron reflectometry) and the other two (9-oxononanoic acid and azelaic acid) will not be deuterated (and thus will not be detectable via neutron reflectometry).

Depending on the makeup of the product monolayer, the measured residue (as a fraction of initial deuterated material) will vary from nothing (signifying a product monolayer made up entirely of azelaic acid and/or 9-oxononanoic acid) to twice the relative amount (the same absolute amount if the same initial surface concentration of oleic acid is assumed) as in the d_{34} case (signifying a product monolayer made up entirely of nonanoic acid).

This experiment was carried out on a pure water subphase at 3 ± 1 °C and the result was intermediate between these two possible extremes. The fraction of deuterated material remaining at the interface was calculated for five ozonolysis reactions and the mean deuterated residue fraction was 9.8 %, with a 95 % confidence interval (assuming sampling from a Gaussian distribution as before) of ± 2.0 % (absolute). The confidence interval here heavily overlaps with the confidence interval for the mean deuterated residue fraction for the d_{34} experiment, so the two values are not significantly different. Indistinguishable fractional deuterated residue means that, from the same oleic acid surface concentration starting point, the deuterated residue present in a d_{18} experiment is half of what it is in a d_{34} experiment. This implies a product monolayer made up of roughly equal molar amounts of nonanoic acid and azelaic and/or 9-oxononanoic acids (the ratio between these latter two cannot be determined by this method, as both are deuterated in a d_{34} experiment and non-deuterated in a d_{18} experiment). While there are limited data available on the temperature dependence of the solubilities of these three products, the solubility of azaleic acid has been reported to reduce to 1.0 g/L at 1 °C from 2.4 g/L at 20 °C (O'Neil, 2006) which suggests that azaleic acid may be lost to the subphase at room temperature while being retained at the air–water interface at near-zero temperatures.

Figure 6 shows a representative example of a time series of 120 s time slices for this reaction on pure water, as well as the reaction on a salt subphase. The absolute amount of deuterated material in the residue is about half of that seen for the d_{34} experiment in the same conditions (see Figure 2), and this comes close to the detection limit for 120-s count times in this neutron reflectometry setup. This results in many non-converging fits for the product monolayer, making its identification via this method of analysis alone difficult. However, taking longer time slices allows for a reliable discernment of a product monolayer, as the quality of the reflectivity statistics scales with the square root of count time (assuming a constant neutron flux). This is also illustrated in the stage-by-stage R vs Q reflectivity plots displayed in Figure S7 in the Electronic Supplement.

A topping-up and re-oxidisation experiment was also carried out with d_{18}-oleic acid, and the results were analogous to those for the d_{34}-oleic acid experiment (except scaled down by a factor of two). This demonstrates that both the nonanoic acid and azelaic/9-oxononanoic acid components of the product monolayer can be built up over time (if only nonanoic acid were to build up, then the build-up of fractional deuterated residue would be faster in the d_{18} experiment; if only azelaic/9-oxononanoic acid were to build up, then no build-up would be observed in the d_{18} experiment). These data are included in the electronic supplement (Figures S9 and S10).

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3.7 Product Elucidation at Near-Zero Temperatures With Partially Deuterated Reactants: Salt Water Subphase

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A series of d_{18} experiments was also run for the salt water subphase at -2 ± 1 °C in which measurable residue was observed for d_{34}-oleic acid ozonolysis. This allowed investigation of the likely makeup of the product monolayer in the same way as under the pure water 3 ± 1 °C conditions. However, the yet lower absolute amounts of residual deuterated material in this experiment posed sensitivity problems for this method of measuring the residue, and therefore the conclusions that can be drawn about the composition of the product monolayer in the salt water -2 ± 1 °C conditions are less secure than those that can be drawn about the composition of the product monolayer on pure water at 3 ± 1 °C discussed above.

In two out of three runs, a residue was detected. This could be because the residue was genuinely absent in the third run, or because it was simply below the detection threshold. Treating the run in which no residue was measurable as a measurement of zero residue yields a mean fractional deuterated residue of 5.6 % with a 95 % confidence interval of ± 2.9 % (absolute) for this system. This may be a slight underestimate of the true value due to the treatment of below-threshold residue as zero residue.

Based on our analysis, the product monolayer cannot be predominantly composed of nonanoic acid, as that would produce a significantly higher fractional deuterated residual in the d_{18} case than in the d_{34} case which can be ruled out by our data. It is not possible to say with confidence that the composition of this product monolayer is similar to that observed in the pure water 3 ± 1°C conditions (a roughly equal mixture of nonanoic acid and azelaic/9-oxononanoic acids), as the data are also consistent with somewhat lower relative levels of nonanoic acid (though not none at all, as that would produce no measurable residue).

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It must be noted that, in this particular case, an assumption had to be made that the reaction would have proceeded to completion within 4000 s, and that anything measured after that point was a stable residue. This is because the residue was, in all these d_{18} salt water -2 ± 1 °C cases, below the detection threshold for a 120 s count time. This meant that the reaction could not be followed to ascertain at which point the system was stable in order to define a period over which the residue could be more accurately measured using a single reflectivity curve compiled over a long count time. As the saltwater trace in Figure 2 (low temperature) shows, the reaction on salt water at low temperatures proceeds to completion over a much longer time frame than the pure water equivalent.

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In order to measure the stable residue, the 120 second interval time series graph is first prepared, and the slope of that graph is then used to determine at what point a stable residue has formed, and the time period during which that graph is flat is then averaged over to create the single "after ozonolysis" reflectivity curve which is shown in the R vs Q reflectivity graphs and used to determine the fractional deuterated residue values. For instance, Figure 2 shows that the signal is no longer declining after 4000 s, so the time period used for the "after ozonolysis" reflectivity curve in Figure S4 is 4000 – 4500 s (heating began at 4500 s). For all fractional deuterated residue calculations except these last (for d_{18} salt water -2 ± 1 °C), the 120 s time series interval graphs have been able to guide the time integration ranges for the step-by-step R vs Q reflectivity curves (see Fig. S7 in the Electronic Supplement).

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However, for the d_{18} salt water -2 ± 1 °C experiment, the absolute signal from the residue was so low that 120 s count times were not sufficient. As a result, the reaction was assumed to have completed by 4000 s (longer than any observed reaction times), and signal was averaged from this point until heating in order to quantify the residue.

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Figures 6 and S8 (in the Electronic Supplement) show a time series and R vs Q reflectivity plots for these conditions. The time series plot demonstrates that any residue is below the detection limit for 120 seconds of counting, however, the 500 seconds over which the "after ozonolysis" reflectivity curve is calculated affords good enough data to discern a residue.

3.8 Atmospheric Product Stability: Temperature Threshold

It has been demonstrated that a residue remains at the interface after ozonolysis (2 h time scale) of an oleic acid monolayer by gas phase ozone at 3 ± 1 °C on a pure water subphase and at -2 ± 1 °C on a 36 g L^{-1} NaCl aqueous solution. However, it would be useful to establish across what ranges of temperature this product monolayer persists.

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In order to investigate this, a product monolayer was gradually heated (1 °C every 5 min) to see if there was a critical ‘threshold temperature’ above which it would be rapidly removed from the interface.

Figure 7 shows the temperature-ramping experiment in detail. The temperature of the subphase is controlled by varying the temperature of a coupled coolant bath. For the experiments discussed thus far, the temperature of the subphase can be measured before each experiment, allowing the offset between bath and subphase to be measured and an accurate assessment of the subphase temperature via direct measurement used for each experiment. For this ramping experiment, it was not practical to measure the subphase temperature directly for every step. Instead, the relationship between bath and subphase temperatures were used to define a linear relationship between bath and subphase temperatures that was deemed sufficiently accurate given the existing ± 1 °C uncertainty. Diurnal temperature variations that could have disturbed this relationship were largely eliminated using air conditioning to maintain the temperature of the experimental area at around 15 °C, which was also key in reducing the impact of condensation. The bath was set to -1 °C for ozonolysis, then increased by 1 °C at t = 1035 s and every 300 s following until 5 °C (corresponding to a measured subphase temperature of 7 °C) was reached after 2535 s. A single step to a bath temperature of 11 °C, which corresponds to a subphase temperature of around 12 °C was performed at t = 3260 s.

This experiment was performed on the FIGARO reflectometer at the ILL (experiment 9-10-1518) and showed that the product film was stable at up to 7 ± 1 °C, though there was a slight linear decay in product monolayer surface concentration with increasing temperature. On further heating to 12 ± 1 °C, no ‘threshold temperature’ was observed but, at this higher temperature, the linear decay ran into the detection limits of the neutron reflectometry setup. This could mean that the monolayer is not stable at or above 12 ± 1 °C, or it could mean that it simply continues to gradually linearly decay with rising temperature above 12 ± 1 °C, but passed the detection limit of the setup used for this experiment. Either way, the product monolayer is certainly stable up to 7 ± 1 °C, but definitely not above 12 ± 1 °C (upper limit).

It is important to note that a monolayer produced at 3 ± 1 °C and then being stable at up to around 12 ± 1 °C does not mean that a reaction carried out at 12 ± 1 °C would definitely produce a stable monolayer. However, this temperature ramping experiment at least provides a hint for the range of temperatures over which these product monolayers might persist. Most of the troposphere is below 10 °C, so these conditions are highly atmospherically relevant.

Hung and Tang (2010) suggested that the physical state of products from the ozonolysis of solid state oleic acid particles by O_3 might be temperature-dependent across a 4 – 9 °C temperature range, and it is worth considering whether the effect we report in present work is linked to this phenomenon, as there is overlap between this transition temperature range and the 6 – 13 °C transition range we observe.

3.9 Kinetic Analysis of Oleic Acid Ozonolysis

Experiments were performed on the FIGARO reflectometer at the ILL (experiment 9-10-1518) to elucidate the effect of temperature changes on the kinetics of the reaction. The ozonolysis reaction was performed with [O_3]$_{gas}$ ranging between 126 ± 15 and 1005 ± 119 ppb. A pseudo-1st-order rate coefficient (k_1) for each reaction was calculated by fitting a modified

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exponential developed in previous work by this group in order to account for the fact that $[O_3]_{gas}$ initially builds up in the reaction chamber and thus rises steeply at the start of the reaction as initial mixing occurs within the chamber (Pfrang et al., 2014). The traditional 1st-order exponential equation that describes a 2nd-order reaction occurring with an excess of one reactant (in this case, O_3) is modified to (Pfrang et al., 2014):

$$\Gamma(t) = \Gamma_0 e^{-k_1\left(t-\frac{v}{f}\left(1-e^{-\frac{f}{v}t}\right)\right)} \tag{3}$$

The expected exponential relationship between surface concentration (Γ) and time (t) is modified by the inclusion of a second exponential function that includes constants for the gas flow rate (f), which is 20 cm^3 s^{-1} for these experiments, and chamber volume (v), which is 2.1×10^3 cm^3, but which requires replacement with an 'effective chamber volume'. The derivation of Eq. (3) is presented in previous work (Pfrang et al., 2014).

It is important to note that this analytical treatment is not a complete description of the processes at work throughout the reaction. Transient reaction products at the interface are, due to their deuterated nature, measured along with the reactant film throughout the reaction if and when they are present (this is why the technique is sensitive to a residual product film). As a result, fitting this analytical model to the data needs to take this into account. A number of assumptions have to be made about the precise way in which ozone mixes into the chamber. These are discussed in detail in Section S3 of the Electronic Supplement. Here, we present and discuss the results of this fitting procedure.

Figure 8 displays fitted k_1 values for reactions under a variety of $[O_3]_{surf}$ conditions at 21 °C and 2 °C, and 95 % confidence intervals for fits of k_2 values ($k_2 = k_1/[O_3]_{surf}$) to these data.

$[O_3]_{surf}$ values were calculated from $[O_3]_{gas}$ values by using a Henry's law solubility constant for O_3 in organics of [organic]/[gas] = 11.7 (unitless) and assuming the same layer thickness of 2 nm. This solubility constant is consistent with the value used previously in ozonolysis experiments by King et al. (2009) and is informed by the work of Smith et al. (2002).

The error in each fitted k_1 value, as noted in Section S3 of the Electronic Supplement, is dominated by uncertainty in model fitting at the start of each reaction. Uncertainty in $[O_3]_{surf}$ arises from uncertainties in the calibration of the pen-ray ozoniser, which was performed using Beer-Lambert law UV absorbance at 254 nm using an extinction coefficient of 1.13×10^{-17} cm^{-2} (Daumont et al., 1992).

The fitted k_2 values for these two conditions (± a 95 % confidence interval) are $(2.2 \pm 0.4) \times 10^{-10}$ cm^2 s^{-1} and $(2.2 \pm 0.2) \times 10^{-10}$ cm^2 s^{-1} at 21 °C and 2 °C, respectively.

Our experiments observe either no difference, or a difference too small to be reliably detected (a difference of < 10 % might not be noticeable given the uncertainty in fitted k_1 parameters and $[O_3]$ calibration). This is a similar situation to that found by Hung and Tang (2010), who observed, for ozonolysis of liquid oleic acid, a very slight dependence on temperature based on their point estimates of reaction rate that was within their margins of error (although they observed a strong temperature-dependence for the ozonolysis of solid oleic acid).

It is important to note that, as this reflectivity-based method for calculating surface concentration of oleic acid is not sensitive only to oleic acid, but also to reaction products that may remain at the interface, it is possible that the rate of reaction does differ across this temperature range, but that changes in product build-up and distribution conspire to entirely mask this, leading to a similar trend in total adsorbed deuterated material at the interface. It seems highly unlikely that counterbalancing effects would conspire to so well balance each other out across a range of [O$_3$] conditions. In any case, from an atmospheric perspective, the key question is not how fast oleic acid reacts, but how fast the monolayer is removed from the interface. These experiments confirm that changing the temperature from room temperature to a more atmospherically realistic near-zero temperature does not notably alter the rate of monolayer removal from the interface.

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Figures 9 shows time series of the product of SLD and thickness for the lowest and highest [O$_3$]$_{surf}$ concentrations used at the two temperatures studied, to provide a clearer visual confirmation of the similar rates of the two reactions.

It can be seen from these two comparisons that the rates of these reactions do not differ appreciably. Indeed, the offset between the two curves is due in both cases to slight differences in starting concentration. These plots also further corroborate the main result of this study – that a residue remains after ozonolysis at near-zero temperature but not at room temperature.

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The rate coefficients determined here are about three times higher than those previously reported for ozonolysis of oleic acid monolayers (King et al., 2009). Significant variability between experiments to determine rates for these heterogeneous reactions is not unprecedented. When Hung and Tang (2010) investigated heterogeneous ozonolysis of liquid oleic acid they measured a rate coefficient that was three times higher than the highest value they could find in previous work (Moise and Rudich, 2002) and up to 10 times higher than the lowest. For solid state ozonolysis, the discrepancy was up to a factor of 40 (Hung and Tang, 2010).

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The most important conclusions here, however, are not the absolute rate coefficients measured but the fact that there is not a notable difference between them. Despite the qualitative differences between the ozonolysis of an oleic acid monolayer at room temperature and more atmospherically relevant near-zero temperatures (namely the presence of a residual monolayer in the latter case), the kinetics of the reaction does not appear to be altered substantially in these two conditions.

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4 Conclusions

4.1 Atmospheric Surface Chemistry

Based on our neutron reflectometry data, we conclude that the ozonolysis of an oleic acid monolayer on a pure water subphase (a basic model of an atmospheric water droplet) does not leave behind a product at the interface at room temperature, but does leave such a residual product film at more atmospherically relevant near-zero temperatures, and may do so at temperatures of up to 7 – 12 °C. Data from an experiment involving re-deposition and re-ozonolysis of oleic acid showing the build-up of this product monolayer convinces us that this is a genuine product of the reaction.

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Further to this, we conclude that the ozonolysis of an oleic acid monolayer film on a 36 gL^{-1} NaCl aqueous solution subphase (a basic model of a sea spray droplet) does not leave a product film at the interface at room temperature, but does leave such a residual product film behind at temperatures below freezing. Such a residual product film probably is not left behind after ozonolysis at the 3 ± 1 °C temperature condition at which stable product films were observed on pure water.

Based on data from experiments performed with a partially deuterated form of oleic acid together with a knowledge of the expected major products of the ozonolysis, we conclude that, for the pure water subphase, this product film is roughly half nonanoic acid, with the other half being azelaic acid or 9-oxononanoic acid, or a mixture of the two. For the salt subphase case, the data are less conclusive on the ratio between these components, though very high or very low fractions of nonanoic acid can be ruled out.

Experiments performed at a variety of O_3 concentrations demonstrate that the rate of monolayer removal does not differ significantly between the two temperatures studied, despite the clear qualitative differences in the end state of the reaction; rate coefficients were determined to be $(2.2 \pm 0.4) \times 10^{-10}$ cm^2 s^{-1} and $(2.2 \pm 0.2) \times 10^{-10}$ cm^2 s^{-1} at 21 ± 1 °C and 2 ± 1 °C, respectively.

4.2 Atmospheric Implications

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Almost regardless of the chemical nature of the surface film, the result from an atmospheric physics perspective is very similar: a film remains at the surface after ozonolysis of an oleic acid monolayer at atmospherically realistic temperatures. The presence of such a film means that the physical effects of a surface monolayer, such as reduced water uptake, reduced surface pressure, and reduced evaporation, will still be present, albeit not to the same extent, as they were in the original oleic acid-coated aerosol droplet. This means the fact that an oleic acid film will oxidise in the atmosphere does not render such a film irrelevant to the physical properties of the droplet in the long term, as would be the case if no residual film remained after ozonolysis.

Furthermore, our re-oxidation experiments demonstrate that an inert product film may build up during the droplet ageing process in the atmosphere, even if only ordinarily short-lived reactive species (such as oleic acid and other unsaturated compounds) were initially emitted into the atmosphere. It is entirely possible that, given suitably cold conditions, an entirely saturated 'full' monolayer could be built up by repeated deposition and ozonolysis of entirely unsaturated precursor surfactants. More generally, long-lived inert films could develop even if only short-lived reactive species are emitted, provided a suitable processing mechanism is available. The ozonolysis of oleic acid studied here is such a mechanism, therefore emissions of oleic acid and similar unsaturated fatty acids may well result in the build-up of saturated monolayers inert to further ozonolysis. This provides a way to reconcile the observation that anthropogenic activity emits significant quantities of unsaturated fatty acids (Shrivastava et al., 2007) with the observation that aerosol particles collected from the atmosphere seem to host monolayers entirely inert to ozonolysis (Jones et al., 2017).

The presence of these long-lived films is atmospherically significant. The surface pressure reduction in particular may have an impact on cloud lifetimes via the stabilisation of lower diameter droplets associated with this change under Köhler theory (Ambaum, 2010). Other possible effects include: reduced water uptake (and therefore growth) of the droplet; inhibited evaporation from the droplet; reduced transfer of species between the droplet and the wider atmosphere (alternative processes leading to this effect have been discussed in earlier work by this research group and others (King et al., 2004; Pfrang et al., 2014, 2017)); and modified surface solubility of other atmospheric species (Barnes, 1997; Benjamin, 1996; Cohen Stuart et al., 1996; Gaines, 1966; Garrett, 1971; Gilman et al., 2004; La Mer, 1962, 1964; Mmereki et al., 2003; Mmereki and Donaldson, 2002; Ray et al., 1991; Rideal, 1924; Tomoaia-Cotisel and Cadenhead, 1991).

In summary, this work provides evidence that even the emission of reactive surfactant species such as unsaturated fatty acids could alter the physical properties of water droplets in the atmosphere (including in clouds) over a much longer timeframe than the atmospheric lifetime of these species would suggest, via the build-up of inert monolayers on the surface of such droplets composed of the products of the oxidative processing of such fatty acids in the atmosphere.

Author contributions

CP and MWAS initiated the research project. CP, MWAS and BW designed the experiments and carried them out. BW analysed the data with support from MWAS and CP. AM (Maestro) provided support during the FIGARO beamtime. AM (Milsom) supported the work during beamtime experiments and off-line calibrations. JT synthesised deuterated oleic acid. BW, CP and MWAS prepared the manuscript.

Data availability

The data presented in this manuscript can be obtained from the corresponding author upon request. The underlying data are archived at ILL and ISIS.

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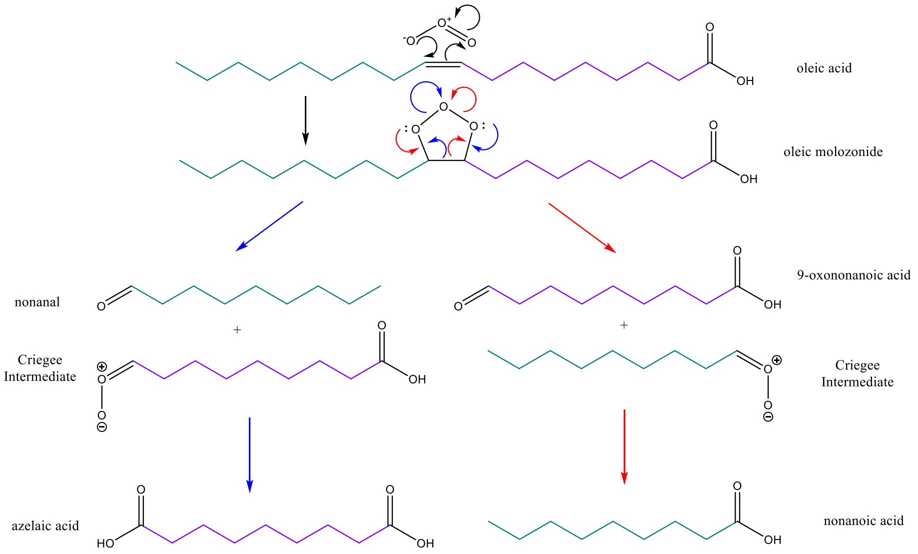

Scheme 1: Oleic acid ozonolysis reaction scheme. We used both fully and half-deuterated oleic acid samples, granting us the ability to create different contrasts for analysis by neutron reflectometry. In the fully deuterated (*d_{34}*) variant of oleic acid, both the head portion (purple) and tail portion (teal) of the molecule are deuterated. In the partially deuterated (*d_{18}*) variant of oleic acid, only the tail portion (teal) is deuterated. The colouring of the products and intermediates indicates the fate of the two portions of the oleic acid molecule, and demonstrates that, when *d_{18}*-oleic acid is oxidised, two products (nonanal and nonanoic acid) are deuterated, and two (ozelaic acid and 9-oxononanoic acid) are not.

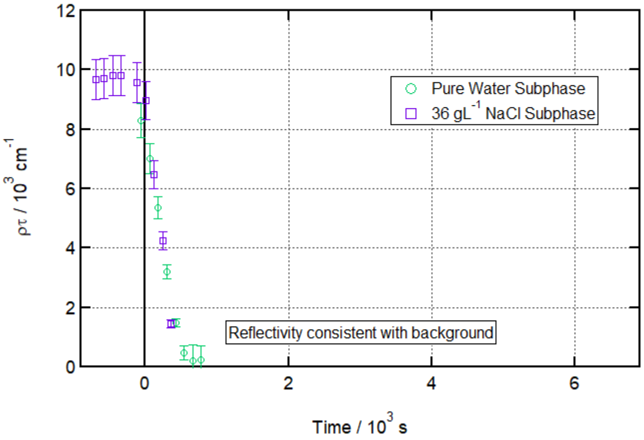

Figure 1: Ozonolysis of an oleic acid monolayer floating on pure vs salt water. Time evolution plot for ozonolysis of 29 µL 1.0 g L^{-1} *d_{34}*-OA (CHCl$_3$ spread. sol.) on pure water (green circles) and 25 µL 1.0 g L^{-1} *d_{34}*-OA 36 g L^{-1} NaCl(aq) (purple squares) subphases by 323 ± 29 ppb O$_3$ introduced at *t* = 0 s at 21 ± 1 °C.

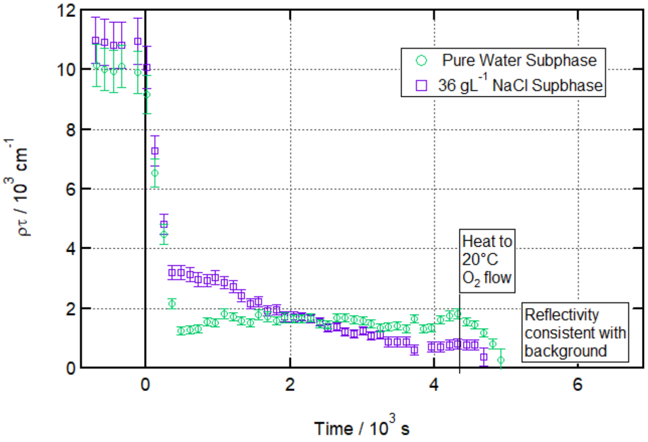

Figure 2: Ozonolysis of an oleic acid monolayer at low temperatures floating on pure vs salt water. Time evolution plot for ozonolysis of 25 µL 1.0 g L^{-1} *d_{34}*-OA (CHCl$_3$ spread. sol.) on pure water (green circles) and 36 g L^{-1} NaCl(aq) (purple squares) subphases by 323 ± 29 ppb O$_3$ introduced at *t* = 0 s at 3 ± 1 °C (pure water) or -2 ± 1 °C (salt water).

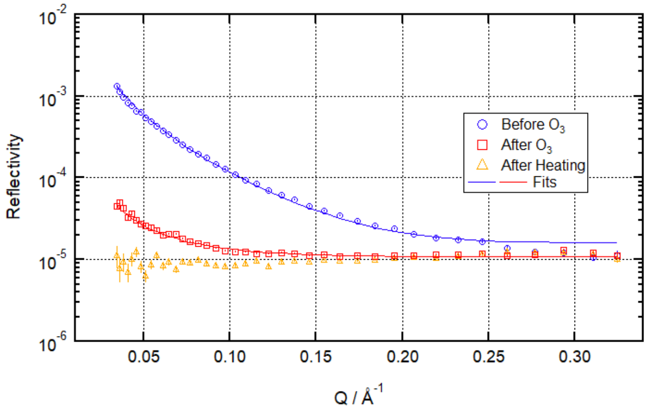

Figure 3: Neutron reflectivity signal from the air–water interface before ozonolysis (blue circles - signal from the pristine oleic acid monolayer), after ozonolysis (red squares - clear signal remaining) and after heating (orange triangles - no measurable signal) for ozonolysis of 25 µL 1.0 g L^{-1} *d*$_{34}$-OA (CHCl$_3$ spread. sol.) on pure water subphase by 323 ± 29 ppb O$_3$ introduced at *t* = 0 s at 3 ± 1 °C.

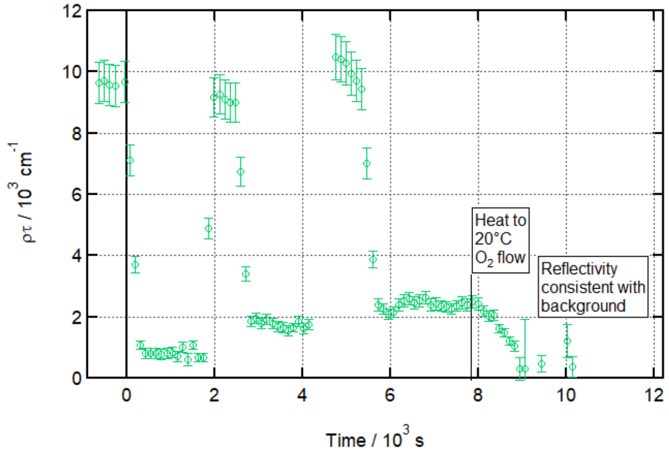

Figure 4: Experiment mimicking an aqueous aerosol droplet exposed to multiple cooking emission peaks and demonstrating the associated build-up of an inert organic film at the air–water interface at low temperatures. Time evolution plot for ozonolysis of 25 µL 1.0 g L^{-1} *d*$_{34}$-OA (CHCl$_3$ spread. sol.) on pure water subphase by 323 ± 29 ppb O$_3$ introduced at *t* = 0 s and after two additional spreadings of 25 µL 1.0 g L^{-1} *d*$_{34}$-OA at 3 ± 1 °C.

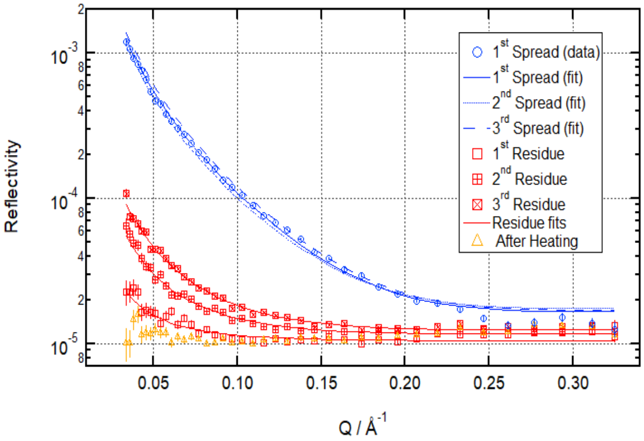

Figure 5: Neutron reflectivity signal from the air–water interface before ozonolysis (blue circles (data only shown for first spreading; fits shown for all three spreadings - clear and consistent signal from the oleic acid monolayers across the three simulated cooking emission peaks), after ozonolysis (red squares-demonstrating the build-up of organic residue at the air–water interface during repeated exposure to cooking emission) and after heating (orange triangles - removal of organic residue at room temperature) for the multi-ozonolysis reaction shown as a time evolution plot in Figure 4.

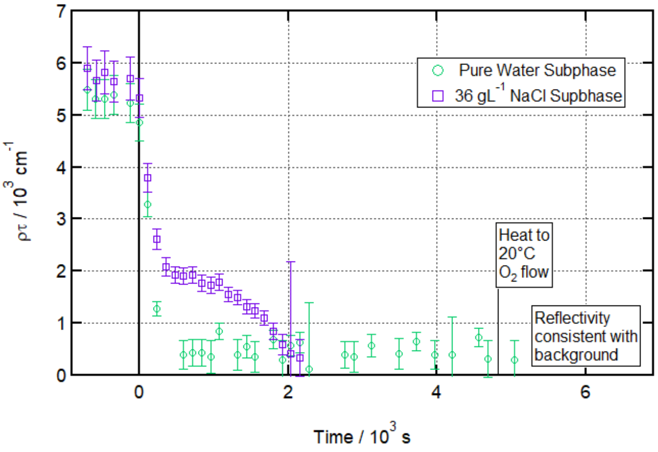

Figure 6: Ozonolysis of a partially deuterated oleic acid monolayer floating on pure vs salt water. Time evolution plot for ozonolysis of 17 µL 1.3 g L^{-1} d_{18}-OA ($CHCl_3$ spread. sol.) on pure water (green circles) and 36 g L^{-1} NaCl(aq) (purple squares) subphases by 323 ± 29 ppb O_3 introduced at $t = 0$ s at 3 ± 1 °C (pure water) or -2 ± 1 °C (salt water).

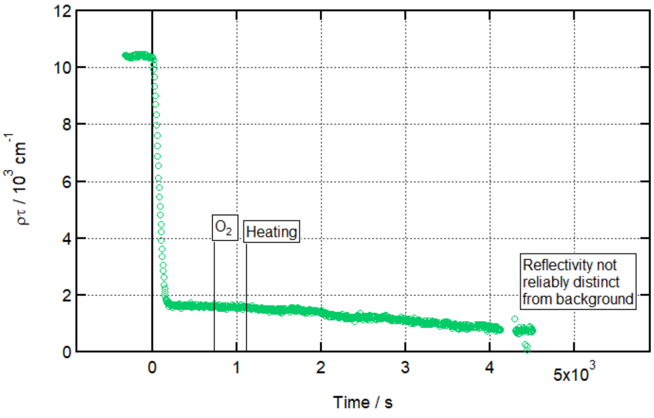

Figure 7: Gradual loss of residue due to increase in temperature. Time evolution plot for ozonolysis of 29 µL 1.0 g L^{-1} d_{34}-OA ($CHCl_3$ spread. sol.) on pure subphase by 754 ± 89 ppb O_3 introduced at $t = 0$ s at 2 ± 1 °C, with temperature ramping (described in detail in the text) from $t = 1035$ s; error bars are omitted for visual clarity.

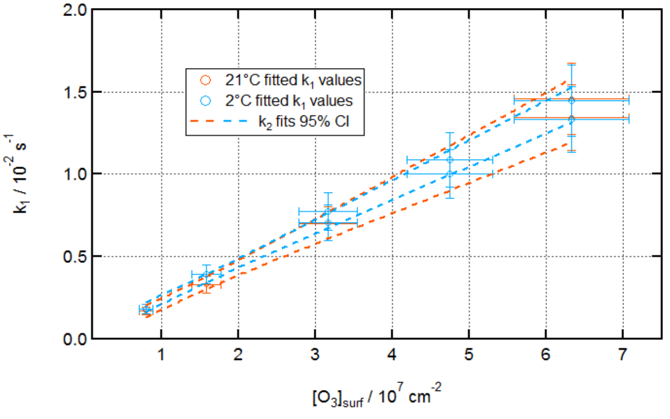

Figure 8: Kinetics of ozonolysis of the oleic acid monolayer on pure water at room and low temperatures. Fitted k_1 pseudo-1st-order rate constants against $[O_3]_{surf}$ at 21 ± 1 °C (orange) and 2 ± 1 °C (aqua).

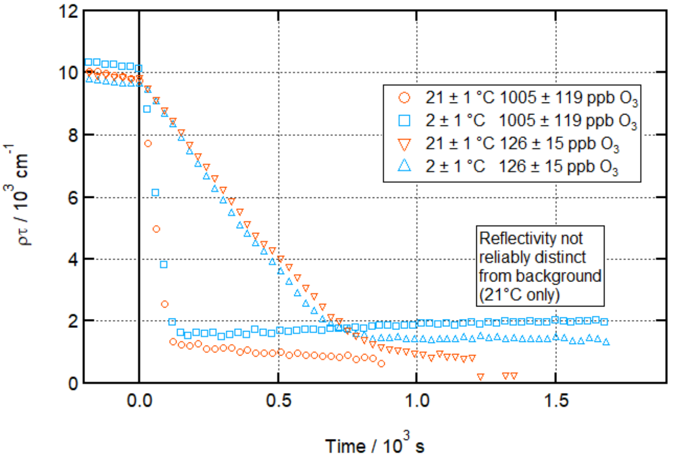

Figure 9: Comparison of time-dependent loss of material from the air–water interface during oleic acid ozonolysis at room and low temperatures and at highest and lowest $[O_3]$. Time evolution plot for ozonolysis of 39 µL 0.75 g L^{-1} d_{34}-OA ($CHCl_3$ spread. sol.) on pure subphase by O_3 introduced at $t = 0$ s at 21 ± 1 °C (orange) and 2 ± 1 °C (aqua); error bars are omitted for visual clarity.

Electronic Supplementary Information

Ozonolysis of fatty acid monolayers at the air–water interface: organic films may persist at the surface of atmospheric aerosols.

Benjamin Woden[1,2], Maximilian W. A. Skoda[2], Adam Milsom[3], Armando Maestro[4], James Tellam[2] and Christian Pfrang[3,5].

[1]Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK
[2]ISIS Neutron and Muon Source, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Didcot, OX11 0QX, UK.
[3]School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK
[4]Institut Laue Langevin (ILL), 71 Avenue des Martyrs, Grenoble, 38000, France.
[5]Department of Meteorology, University of Reading, Whiteknights Road, Reading, RG6 6BG, UK.
Correspondence to: Christian Pfrang (c.pfrang@bham.ac.uk)

Section S1 – Monolayer Characterisation at Low Temperature

In order to ensure that the system could effectively be modelled as a monolayer for neutron reflectometry data fitting, and to find an optimum spreading volume that packs in a similar manner across the temperature ranges studied (to ensure that temperature effects alone, rather than effects due to monolayer phase, were studied), monolayers of oleic acid were spread on pure water and 0.6 M NaCl solution subphases at room temperature, just above and just below ice melting point (not accessible for pure water) and Wilhelmy tensiometric measurements were performed using a Langmuir trough equipped with a NIMA surface pressure sensor and control software. π-A isotherms were recorded and are shown below in Figures S1 and S2.

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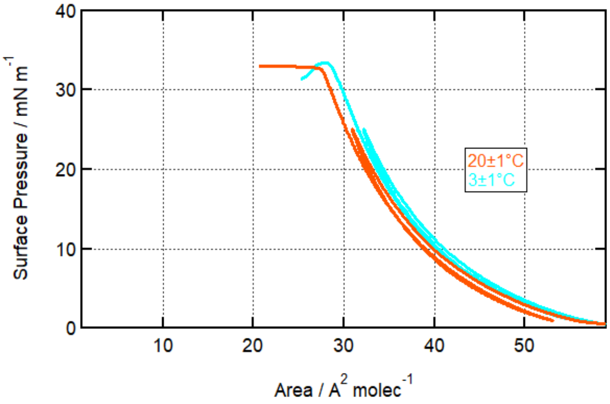

Figure S1: π-A Isotherm for oleic acid on pure water at 3 °C (aqua) and 20 °C (orange).

These tensiometry experiments showed that the system could be described as a well-behaved monolayer over the temperature range of interest on pure water and NaCl solution.

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The impact of temperature on the π-A isotherm for oleic acid was not large, and indeed was not reliably distinguishable from zero by our apparatus and method. Due to this, the target surface area per molecule of 30 Å^2 used for previous experiments at room temperature was deemed suitable for use at the lower temperature as well. This choice of initial surface concentration maximises initial signal for neutron reflectometry and infrared spectroscopy measurements without risking film breakage.

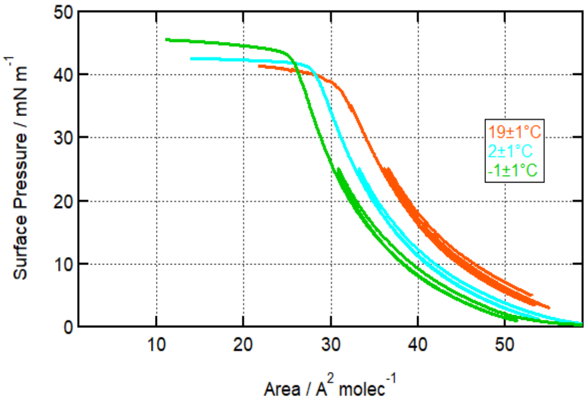
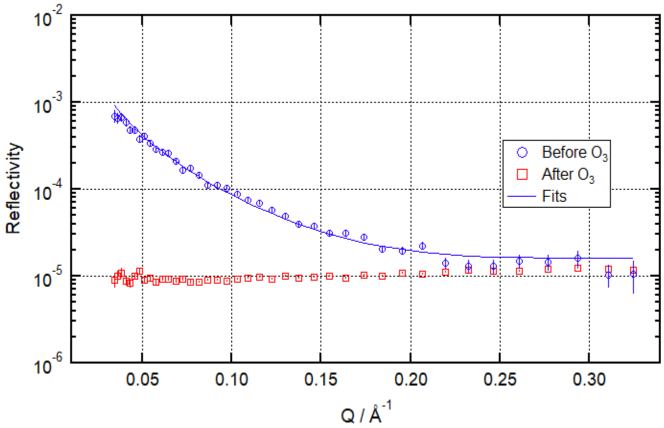


Figure S2: π-A Isotherm for oleic acid on 36 g L^{-1} NaCl at -1 °C (green), 2 °C (aqua) and 19 °C (orange).

The situation on the NaCl solution subphase was somewhat different. Compared with the pure water condition, significantly higher surface pressure regimes are accessible before the breaking of the monolayer at all temperatures and these are associated in the low temperature conditions with slightly higher surface concentrations. There is an observable trend of lower surface pressure with lower temperature at a given surface concentration, and this trend does not appear to be linear. These results are consistent with earlier findings by Knopf and Forrester (2011).

Based on these results, the target surface area per molecule of 30 Å^2 used for the pure water condition was extended to the NaCl solution condition at all temperatures. Preserving consistency across conditions and maximising observable signal were considered highly important, and the slight risk of overspreading in the room temperature NaCl solution condition (which was not observed during experiments) was deemed acceptable to achieve this, particularly as preliminary neutron reflectometry data gathered with an early prototype of the apparatus (ISIS INTER reflectometer; RB 1710483) had suggested that this was the least interesting of the new conditions under study.

Section S2 – Reflectivity Curves



60 **Figure S3: Reflectivity before ozonolysis (blue circles), and after ozonolysis (red squares) for ozonolysis of 29 µL 1.0 g L^{-1} *d*$_{34}$-OA (CHCl$_3$ spread. sol.) on pure water subphase by 323 ± 29 ppb O$_3$ introduced at *t* = 0 s at 21 ± 1 °C.**

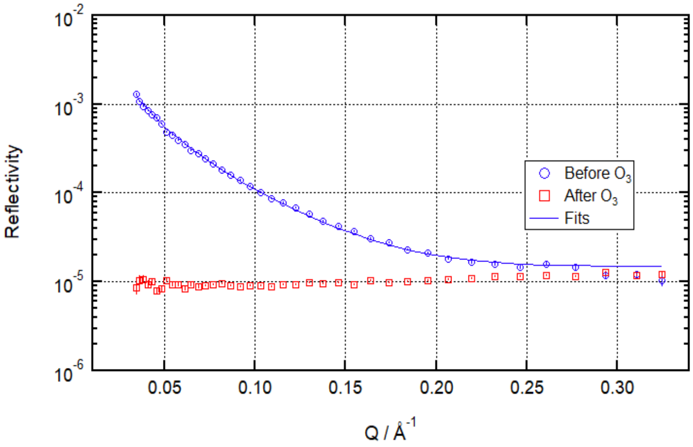
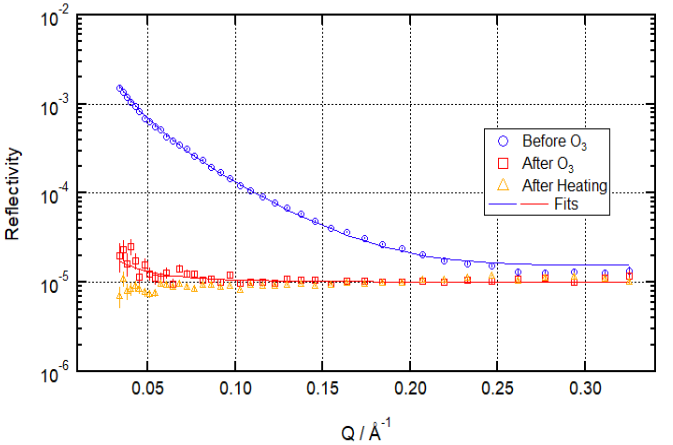
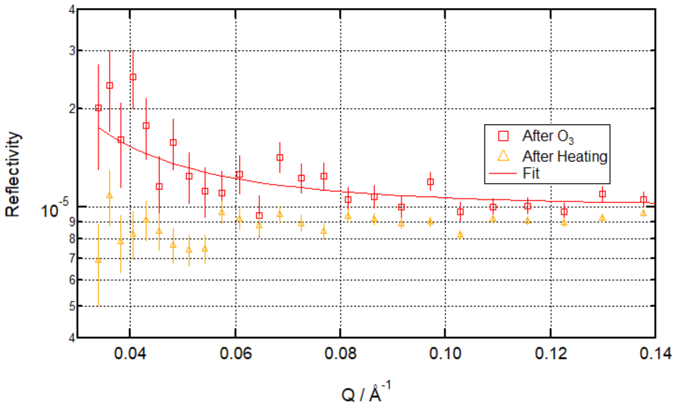


Figure S4: Reflectivity before ozonolysis (blue circles), and after ozonolysis (red squares) for ozonolysis of 25 µL 1.0 g L^{-1} *d*$_{34}$-OA (CHCl$_3$ spread. sol.) on 36 g L^{-1} NaCl(aq) subphase by 323 ± 29 ppb O$_3$ introduced at *t* = 0 s at 21 ± 1 °C.



(a)



(b)

Figure S5: (a) Reflectivity before ozonolysis (blue circles), after ozonolysis (red squares) and after heating (orange triangles) for ozonolysis of 25 µL 1.0 g L^{-1} d_{34}-OA ($CHCl_3$ spread. sol.) on 36 g L^{-1} NaCl(aq) subphase by 323 ± 29 ppb O_3 introduced at $t = 0$ s at -2 ± 1 °C; (b) zoomed in Fig. S5(a) to illustrate the clear presence of a residue (red squares) that is lost upon heating (orange triangles).

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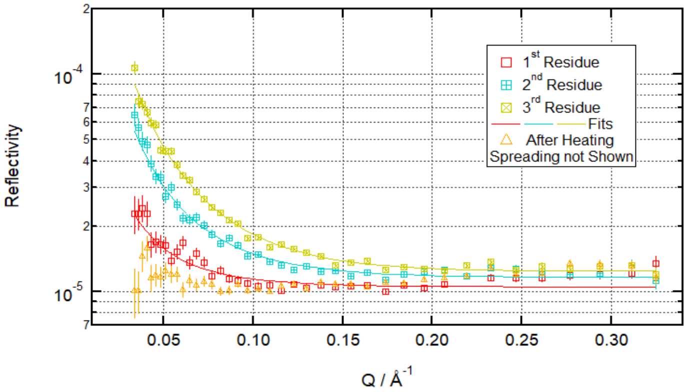

Figure S6: Reflectivity after ozonolysis from the first (open red squares), second (teal squares with an upright cross), and third (olive squares with a diagonal cross) ozonolysis steps, and after heating (orange triangles) for the multi-ozonolysis reaction shown in Figures 4 and 5 (main paper).

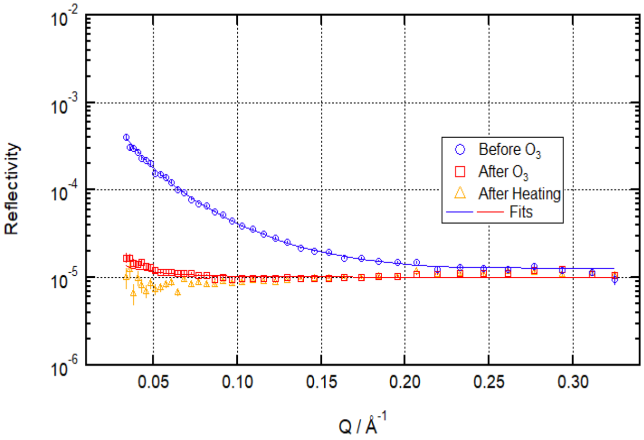

Figure S7: Reflectivity before ozonolysis (blue circles), after ozonolysis (red squares) and after heating (orange triangles) for ozonolysis of 17 µL 1.3 g L^{-1} d_{18}-OA (CHCl$_3$ spread. sol.) on pure water subphase by 323 ± 29 ppb O$_3$ added at t = 0 s at 3 ± 1 °C.

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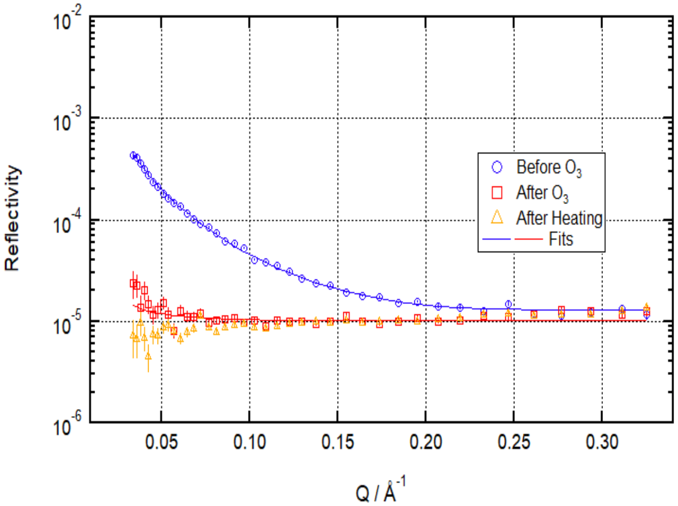

Figure S8: Reflectivity before O_3 (blue circles), after O_3 (red squares) and after heating (orange triangles) for ozonolysis of 17 µL 1.0 g L^{-1} d_{18}-OA ($CHCl_3$ spread. sol.) on 36 g L^{-1} NaCl(aq) subphase by 323 ± 29 ppb O_3 added at t = 0 s at 3 ± 1 °C.

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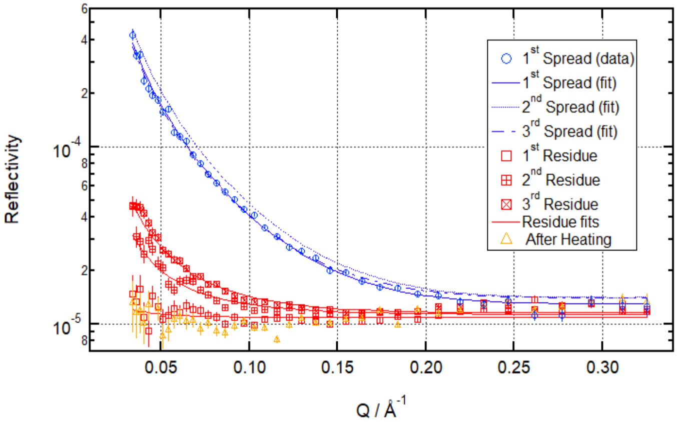

Figure S9: Reflectivity before ozonolysis (blue circles (data only shown for first spreading; fits shown for all three spreadings), after ozonolysis (red squares) and after heating (orange triangles) for a multi-ozonolysis reaction (analogous to that shown in Figures 4 and 5 (main paper) and S6) of 17 µL 1.0 g L^{-1} d_{18}-OA at 3 ± 1 °C.

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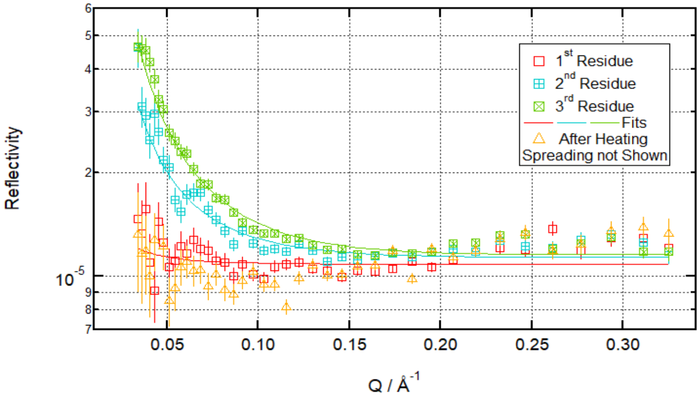

Figure S10: Reflectivity after ozonolysis from the first (open red squares), second (teal squares with an upright cross), and third (olive squares with a diagonal cross) ozonolysis steps, and after heating (orange triangles) for the multi-ozonolysis reaction shown in Figure S9.

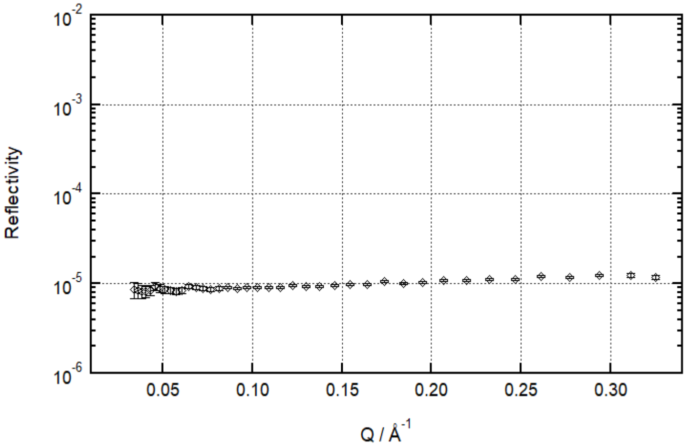

Figure S11: Reflectivity for a pure null-reflecting air–water interface.

Section S3 – Kinetic Fitting

In the latter stages of the reaction, reflectometry signal from products is likely to be a significant or even dominant contributor to reflectivity. Indeed, the primary case made in this paper is that we can use residual reflectivity that cannot be depressed by further ozonolysis at low temperatures to infer the presence of a residual monolayer of reaction products. As a result, we do not attempt to fit data for lower surface coverage values than 10^{14} cm^{-2} (as calculated by fitting reflectivity curves and assuming all reflectivity is due to oleic acid). This represents approximately the final third of the reaction in terms of reflectivity, and was chosen as it is at this point that significant deviations from a smooth, regular function are observed from a basic visual appraisal of the data. However, even before this point, some of the measured reflectivity will be due to the presence of reaction products at the interface (whether or not they are sufficiently stable to persist at the end of the reaction), meaning that calculations of oleic acid surface coverage will be over-estimations to some degree as soon as the reaction begins, and to a greater and greater extent as the reaction progresses. As a result, fitted pseudo-1st-order rate constants are likely to be slight under-estimations, even when the latter third of the reaction is excluded from the fitting.

Another complication involves the mixing of O_3 into the chamber at the very start of the reaction. The model presented in equation 1 assumes that $[O_3]_{gas}$ is uniform throughout the reaction chamber. This is, in reality, not the case. O_3 is introduced to the chamber through a long tube running down one size of the chamber just above the air/water interface with holes of varying diameters drilled along its length. This oxidant gas ingress system was designed by a previous member of this research group in order to achieve even distribution of the oxidant gas with respect to the long edge of the interface (it is unavoidably still the case that there is a concentration gradient across the short edge) and the precise sizes of the drilled holes were tuned in order to achieve even mixing based on fluid dynamics simulations (Sebastiani, 2014; Sebastiani et al., 2015). The mixing time for the cell is estimated as around 60 s. As a result of this, $[O_3]_{gas}$ will rise much more quickly in a boundary layer just above the air/water interface at around the height of the ingress pipe than it will in the chamber as a whole. It is, of course, the $[O_3]_{gas}$ just above the interface that is relevant for the progress of the reaction. This boundary layer constitutes an 'effective volume' for the reaction which is significantly lower than the total volume of the reaction chamber. Determining the volume of this boundary layer is not experimentally possible, and its value is unfortunately something of a fudge factor in fitting rate constants to these data. Assuming too high an effective volume will mean that the model underestimates the time it takes for the reaction to 'get up to speed', meaning that too high a rate constant will be fitted to compensate.

Usefully, this effect scales with $[O_3]_{gas}$. Choosing too high an effective volume (for instance by using the entire chamber volume of 2.1×10^3 cm^3) results in very poor fitting at higher values of $[O_3]_{gas}$, and causes fitted k_1 values to show a superlinear relationship with $[O_3]_{surf}$, meaning no 2nd-order rate constant can be determined. Choosing too low an effective volume results in very poor fitting at lower values of $[O_3]_{gas}$ and a sublinear relationship between k_1 and $[O_3]_{surf}$. It is possible, therefore, to estimate a boundary layer volume by appraising both the quality of fits between model and data at various values of $[O_3]_{surf}$, and by assessing the relationship between k_1 and $[O_3]_{surf}$, which should be linear (due to the 2nd-order nature of the reaction). As long as the same boundary layer is used, fitted parameters from different experiments will be meaningfully comparable.

For this work, a boundary layer volume of 35 cm^3 (or a boundary layer height above the interface of 2 mm) was used, as it was appraised to produce a reasonable quality of fit for experimental data across the range of $[O_3]_{gas}$ conditions studied, and produced suitably linear relationship between k_1 and $[O_3]_{surf}$ in order for a 2nd-order rate constant (k_2) to be calculated.

This is further complicated due to experimental uncertainty regarding the exact time of the start of the reaction. The reaction is started by manually uncovering part of the UV lamp inside the ozoniser, and the moment at which this action is performed is treated as t_0 for that reaction. However, this manual process is only as precise and reproducible as the finger movements required to perform it. Sometimes, the lamp might be uncovered more slowly than others. Sometimes, the sheath might stick slightly, delaying the uncovering of the lamp by a second or two. Sometimes, the experimenter might overshoot the desired sheath position, uncovering slightly more of the lamp than intended for a fraction of a second. The situation is yet further complicated by the fact that the 'head' of O_3 produced still has to travel a few metres down the tube before it enters the chamber.

When fitting this kind of exponential function, the first few points exercise a high degree of leverage over the whole fit. However, it is exactly these first few points (reflectivity data are collected in 5 second frames for these experiments) that suffer from this uncertainty over the precise start time of the reaction. In order to overcome this difficulty, the first three points (15 seconds) of each reaction are not fitted, and a time offset parameter is added to the model (each instance of "t" on the right-hand-side of equation 2 is replaced by a "$(t-t_{offset})$" term). This produces the problem that t_{offset} is somewhat correlated with Γ_0 – the reaction can be modelled to have started arbitrarily far back into the past before the fitted data as long as the starting surface coverage is raised to correspondingly high and physically unrealistic values. In order to avoid this, Γ_0 is measured before the reaction begins (under a stream of O_2 containing no O_3) and the parameter is fixed for each fitting based on this measurement. Fitting then proceeds by allowing k_1 and t_{offset} to vary, and fits are achieved by this method that tend to converge on values of t_{offset} (generally 10 – 20 s) that make physical sense.

Variation in the assumptions outlined above result in good agreement between model and data for each experiment and produce k_1 values that differ by as much as 15 % from the values produced via the fitting methods settled upon. This error (which is far greater than the error associated with reflectivity fitting at each individual point, and therefore dominates the error in fitted k_1 values) is reflected in our final calculated values for the 2nd-order rate constant.

This error due to model subjectivity turned out to have a much greater effect on the robustness of the fitted k_1 values than did the first problem discussed here (that of deciding what portion of the end of the reaction to discard from fitting due to overbearing influence on fitted surface coverage values of reflectivity due to reaction products). The choice of where to stop fitting made much less difference to the resultant fit than did the choice of where to start fitting and what boundary layer volume to use.

This analytical fitting process does involve the piling of several epicycles upon the basic model of a 2nd-order reaction in which one component in excess, producing a series of pseudo-1st-order reactions with rate constants proportional to the concentration of the excess component. Particularly with regard to the $[O_3]_{gas}$ gradient at the start of the reaction, these epicycles are somewhat arbitrary and depend on human judgement in terms of assessing linearity of the 2nd-order plot and goodness of fit of the 1st-order plots. The problem could be avoided by using a numerical model to explicitly represent the surface concentrations of oleic acid and all likely deuterated products and intermediates and the rates at which those products and intermediates are produced, decay, and partition away from the surface into the bulk phase or gas phase, as well as to explicitly represent the spatial and temporal gradients of $[O_3]_{gas}$ within the chamber. Several numerical models focusing on the first part of this (explicitly dealing with various transient species and products at the interface, as well as in multiple layers) are under development by this research group in collaboration with others, and their use has already yielded significant contributions in the field of aerosol kinetics (Pfrang et al., 2010, 2011; Sebastiani et al., 2018; Shiraiwa et al., 2010, 2012).

However, a full investigation of the detailed kinetics of this reaction is considered out of scope for this study, as it has been studied before (King et al., 2009), and the primary purposes of this work is to investigate differences between the reaction at room temperature and at a more atmospherically realistic near-freezing temperature. As is made clear in the presentation of the results of this kinetic fitting in the main text, this simpler analytic approach demonstrates that there is not a significant difference in the kinetics of the reaction between these two temperature conditions. As a result, it was not considered worthwhile to deploy the numerical model in order to attempt to account for the slight systematic bias towards underestimation of rate constants present in the analytical model, as it would be exceedingly unlikely to uncover anything of further interest.

Figure S12 shows an example of equation 2 fitted to a kinetic time series as described above.

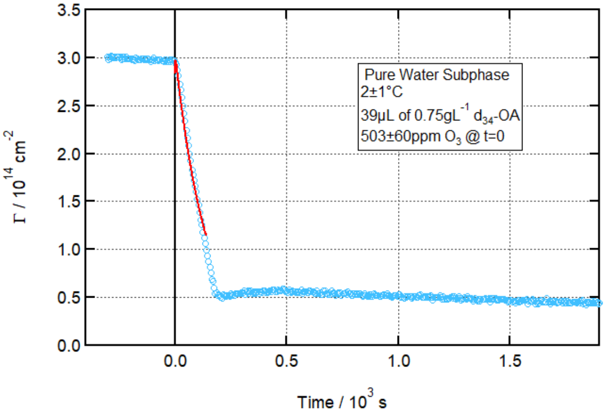

Figure S12: Time evolution plot for ozonolysis of 39 µL 0.75 g L^{-1} *d*$_{34}$-OA ($CHCl_3$ spread. sol.) on pure water subphase by 503 ± 60 ppb O_3 introduced at *t* = 0 s at 2 ± 1 °C showing Eq. (2) (main paper) fitted to the data; error bars omitted for visual clarity.

Section S4 – IRRAS Data

As mentioned in the method section, this work was carried out in a reaction chamber designed for the integration of simultaneous *in situ* IRRAS measurements on a neutron reflectometry beamline. This equipment was deployed and used for the experiments carried out on INTER, but could not be deployed on FIGARO due to space restrictions. IRRAS integration is primarily intended to facilitate the study of mixed monolayers, in which one component can be deuterated (for neutron reflectometry) and the other left non-deuterated (and thus easily measurable by IRRAS). As the work discussed here focused entirely on single-component monolayers, the IRRAS data did not provide any additional insight. IRRAS can also measure deuterated components (the IR absorbance bands are shifted to a lower wavenumber, distinguishing them from the absorbance bands associated with non-deuterated components), but the sensitivity in this region is much lower, as these bands are weaker and more affected by atmospheric interference. This means that IRRAS measurements cannot distinguish the residues left at low temperatures from background noise. Figure S13 shows an example of IRRAS data from an ozonolysis experiment on INTER.

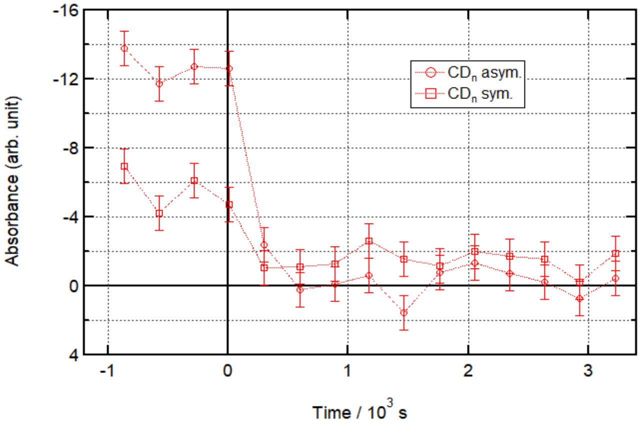

Figure S13: Time evolution plot for ozonolysis of 29 µL 1.0 g L^{-1} d_{34}-OA (CHCl$_3$ spread. sol.) on pure subphase by 323 ± 29 ppb O$_3$ introduced at t = 0 s at 21 ± 1 °C showing integrated IR absorbance for CD$_n$ asymmetric (circles) and symmetric (squares) bands.

Section S5 – Stability Run

In order to ensure that the monolayer was stable at low temperatures, and that the reactions observed were chemical oxidation on the introduction of O$_3$, and not confounded by significant loss of material through physical or chemical processes unrelated to ozonolysis, a long exposure of an oleic acid to a pure O$_2$ flow was performed, and the results are shown in Figure S14 below.

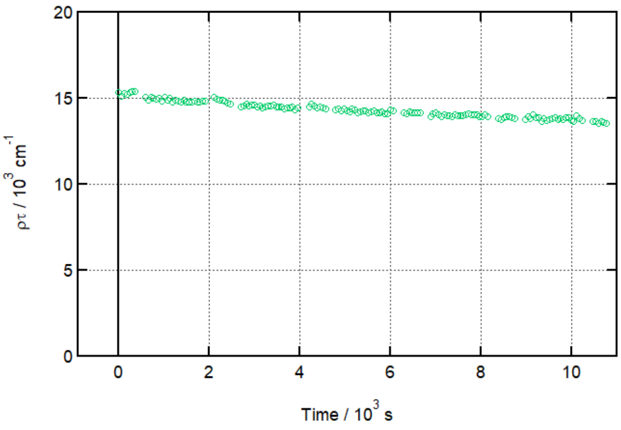

Figure S14: Stability run; time evolution plot for 30 µL 1.2 g L^{-1} *d*$_{34}$-OA (CHCl$_3$ spread. sol.) at 3 ± 2 °C on pure water subphase under pure O$_2$ flow; error bars omitted for visual clarity. $\rho\tau$ is the product of neutron scattering length density and layer thickness is it proportional to the surface excess $\Gamma = \frac{\tau\rho}{b}$, where *b* is the scattering length of the molecule (*d*$_{34}$-OA).

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References

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