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Oxidation by Ozone of Linoleic Acid Monolayers at the Air–Water Interface in Multi-Component Films at 21 °C and 3 °C.

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Abstract

Aqueous aerosols are often covered in thin films of surface-active species, such as fatty acids which are prominent components of both sea spray and cooking emissions. The focus of our study are one-molecule thin layers of linoleic acid (LOA) and their behaviours when exposed to ozone in multi-component films at the air–water interface. LOA's two double bonds allow for ozone-initiated autoxidation, a radical self-oxidation process, as well as traditional ozonolysis. Neutron reflectometry was employed as highly sensitive technique to follow the kinetics of these films in real time in a temperature-controlled environment.

We oxidised deuterated LOA (*d*-LOA) as a monolayer, and in mixed two-component films with either oleic acid (*h*-OA) or its methyl ester, methyl oleate (*h*-MO), at room temperature and atmospherically more realistic temperatures of 3 ± 1 °C. We found that the temperature change did not notably affect the reaction rate (ranging from 1.9 to 2.5×10^{-10} cm² s⁻¹) which was similar to that of pure OA. We also measured the rate coefficient for *d*-OA/*h*-LOA to be $2.0 \pm 0.4 \times 10^{-10}$ cm² s⁻¹. Kinetic multi-layer modelling using our Multilayer-Py package was subsequently carried out for further insight. Neither the change in temperature nor the introduction of co-deposited film components alongside *d*-LOA consistently affected the oxidation rates, but the deviation from a single process decay behaviour (indicative of autoxidation) at 98 ppb is clearest for pure *d*-LOA, weaker for *h*-MO mixtures and weakest for *h*-OA mixtures. As atmospheric surfactants will be present in complex, multi-component mixtures, it is important to understand the reasons for these different behaviours even in two-component mixtures of closely related species. The rates we found were fast compared to those reported earlier. Our work demonstrates clearly that it is essential to employ atmospherically realistic ozone levels as well as multi-component mixtures especially to understand LOA behaviour at low O₃ in the atmosphere. While the temperature change did not play a crucial role for the kinetics, residue formation may be affected, potentially impacting on the persistence of the organic character at the surface of aqueous droplets with a wide range of atmospheric implications.

1 Introduction

Many anthropogenic and biogenic organic compounds emitted into the atmosphere show surfactant activity and therefore can partition to the air–water interfaces that form the surfaces of atmospheric droplets.¹⁻³ Aqueous aerosols are thus often covered in thin films of surface-active species, such as fatty acids which are prominent components of sea spray and cooking emissions. Various properties of these films and their reactivity has been probed mainly for simple fatty acids,⁴⁻⁸ while less work has focussed on polyunsaturated fatty acids such as linoleic acid (LOA) which is the main focus of the present study.

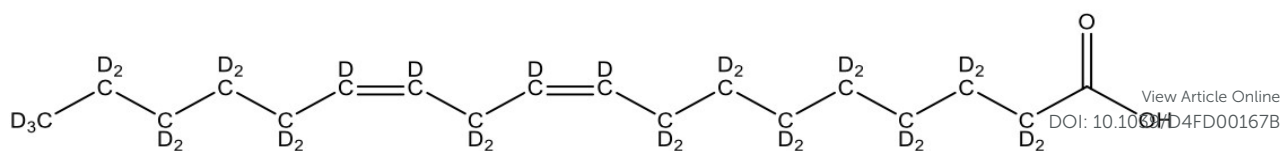
The oxidation of these organic species to form secondary organic aerosol (SOA) has been studied extensively in the past,⁹⁻¹² and the SOA thereby produced will have climatic cloud lifetime effects. However, the partitioning of these species into monolayers at the surfaces of cloud droplets has also been observed to affect their reactivity.^{4-6,13} Perhaps more significant, though, may be the effects that the presence of a surface monolayer has on the cloud droplets themselves. Cloud formation, growth, evaporation, and rainout processes have a critical dependence upon surface tension as a result of the



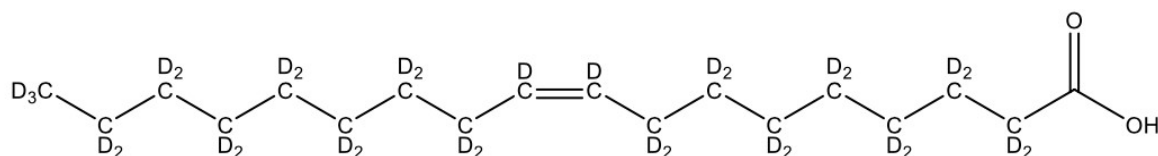


53 Kelvin effect.¹⁴ The presence of insoluble organic films at the air–water interface has a lowering
54 effect on the surface tension of the resultant water aerosols, with impacts on interactions with clouds,
55 and with cloud lifetime effects.³ The lowering of the surface tension associated with the presence of
56 a monolayer would seem, via a weakening of the Kelvin effect, to suppress the destabilisation of small
57 droplets and resultant suppression of nucleation that the Kelvin effect produces.
58 On this basis, the presence of these surfactants on aerosols could promote nucleation via reducing the
59 surface tension of the droplets thereby nucleated. Additionally, the presence of such monolayers on
60 the surface of existing droplets enhances their stability at lower diameters. This enhancement of
61 nucleation and comparative stabilisation of lower diameter droplets could lead to increased cloud
62 lifetimes.
63 There are also several other routes via which the presence of a monolayer film on the surface of a
64 cloud droplet has important consequences for atmospheric chemistry. On the one hand, such films
65 can act as a barrier to mass transport between the water droplet and the atmosphere. Many studies
66 have shown that insoluble films at the interface are able to significantly retard both the evaporation
67 of the water droplet itself and the transport of oxygen (O₂), ozone (O₃), ammonia (NH₃), and many
68 other important atmospheric species between the water droplet bulk phase and the atmospheric bulk
69 phase.^{15–22} This inhibition of cross-interfacial transport could hinder the progress of atmospheric
70 reactions inside aqueous aerosols that rely heavily on mass-transport steps across the air–water
71 boundary.²³
72 On the other hand, the surface film itself can act as a ‘2D solvent’ for species from the atmosphere,
73 thus allowing the dissolution of species that would not normally dissolve in a water droplet, or altering
74 the solvation behaviour of species that normally would dissolve in the aqueous droplet.^{24–28} This effect
75 may play an important role in the transport of various species by water droplets, as it allows species
76 that would not normally be transported by water droplets to be adsorbed at the coated interface.³
77 These changes in solvation behaviour at the interface could impact the rates and even nature of
78 atmospheric reactions that occur heterogeneously at the surface of such particles. Studies of some
79 reactions have shown a reduction in rates, such as the rate of production of nitric acid (HNO₃) from
80 dinitrogen pentoxide (N₂O₅) and water^{29,30} as a result of the presence of these coatings³ which is a
81 key atmospheric process for the redistribution of nitrogen amongst various species in the atmosphere.
82 In summary, the reactivity and properties of these surfactant films deserve further study, as they likely
83 have a vast range of effects that are of climatic and meteorological significance, be that by affecting
84 the reactivity of the film components and associated SOA production, by weakening the Kelvin effect
85 and thus extending the lifetime of reflective clouds, or by modifying key atmospheric chemical
86 processes that involve adsorption to the surface of or diffusion into the bulk of water droplets.
87 The by far most commonly studied unsaturated fatty acid in the context of atmospheric aerosol
88 coatings is oleic acid (OA).^{e.g.5,6,31,32,33,34} OA will react with highly reactive gas-phase species in the
89 atmosphere such as O₃,^{5,32,33,35} OH³⁴ and NO₃.^{6,31} OA’s single double bond limits the complexity of
90 potential products being formed making it a fairly well-understood model system for ozone
91 interaction with atmospheric surfactants.^{e.g.36} The poly-unsaturated analogue of OA, linoleic acid
92 (LOA), represents a logical next step for investigations.
93 The focus of the study presented here are one-molecule thin layers of linoleic acid (LOA) and their
94 behaviours when exposed to ozone in multi-component films at the air–water interface. LOA contains
95 two double bonds allowing for ozone-initiated autoxidation, a radical self-oxidation process, as well
96 as traditional ozonolysis.^{37,38} The core of the experiment involved studying the oxidation of custom-
97 deuterated LOA (*d*-LOA) as a pure monolayer, and in mixed monolayers with oleic acid (*h*-OA) and
98 methyl oleate (*h*-MO; the methyl ester analogue of OA) at both room temperature and a more
99 atmospherically relevant temperature of 3 ± 1 °C. The OA/LOA system was also studied in a reverse
100 deuteration configuration (*d*-OA/*h*-LOA) in both these temperature conditions. Exploratory data from
101 *d*-LOA/stearic acid (*h*-SA; the saturated analogue of OA) mixed monolayers was also gathered. The
102 custom-deuterated surfactants employed in the present study are displayed in Fig. 1.

103



(a)



(b)

Figure 1 – Custom-deuterated surfactant molecules employed in the present study: (a) deuterated linoleic acid (*d*-LOA); and (b) deuterated oleic acid (*d*-OA).

Compared to OA reactivity, there has been fairly little previous work on the oxidation of LOA by ozone: He et al.³⁹ studied a different LOA morphology and used much higher ozone concentrations than found in the atmosphere; Chu et al.³⁷ suggested that competing LOA reaction mechanisms dominate under different ozone conditions.

2 Methodology

The experiments involved oxidation of custom-deuterated LOA (*d*-LOA) as a monolayer, and in mixed two-component films with hydrogenated oleic acid (*h*-OA) or its methyl ester, methyl oleate (*h*-MO), at room temperature (21 ± 1 °C) and atmospherically more realistic temperatures of 3 ± 1 °C. We also carried out initial experiments on mixed monolayers containing deuterated oleic acid (*d*-OA) and linoleic acid (*h*-LOA) to establish the possible impact of the linoleic acid co-deposition on the well-established reactivity of oleic acid towards ozone. The oxidation of the surfactant films was followed at ozone levels of less than 100 ppb to ca. 1 ppm. Neutron reflectometry (NR) was employed as a highly sensitive technique to follow the kinetics of these films in real time in a temperature-controlled environment. Below, the experimental set-up is outlined first, before briefly introducing the neutron reflectometry method followed by the multi-layer modelling analysis.

2.1 Experimental Set-up

The experimental set-up has been described previously (Woden et al., 2021;³³ compare also Skoda et al., 2017⁴⁰ and Woden et al., 2018⁴¹ for earlier variations of the set-up for study of related systems) and is only briefly outlined here. All experiments were performed on the specular neutron reflectometry instruments INTER at the ISIS Neutron and Muon Source.

A custom-built aluminium gas flow cell (volume of ca. 1.5 L) was fitted with a PTFE liquid trough (inner dimensions of 238 mm × 70 mm). This reaction chamber was mounted on the sample stage and interfaced with the gas delivery system. The trough was filled with 90 mL of null-reflecting water (NRW). 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 ca. 2-hour experiment were always less than 0.15 mm for a water height of ca. 5 mm in the trough. The chamber was designed to provide a controlled and confined environment in which monolayers can be oxidised by a gas-phase oxidant while under analysis by both neutron reflectometry and infra-red reflection absorption spectroscopy (IRRAS) as described in detail in a method paper.⁴⁰ For the present study, a further iteration of the sample environment development was deployed to allow for cooling of the subphase, in order to access relevant atmospheric temperature conditions (compare Woden et al., 2021).³³ Because of the low relative humidity (RH) used in the work presented here, we did not observe any condensation within the reaction chamber or on the windows throughout the experiments even at near-freezing temperatures (3 ± 1 °C).



141 Monolayers were spread using 20–40 μL of the spreading solutions in chloroform, leaving a
142 monolayer of the dissolved species after solvent evaporation. Dry oxygen was continuously flowing
143 (flow rate: 1.2 L min^{-1}) into the chamber to provide a low ($< 10 \%$) RH environment and to avoid
144 build-up of any gas-phase products. Data were recorded for several minutes before ozone (O_3) was
145 admitted into the chamber. O_3 was generated by exposing the O_2 flow to UV light using a commercial
146 PenRay ozoniser (UVP Ltd, Cambridge) to ozonise the stream of O_2 (99.999 %; BOC Ltd) regulated
147 by an electronic mass flow controller to achieve O_3 mixing ratios in the range of 98–983 ppb; the
148 ozoniser was calibrated offline using UV–Vis absorption at 254 nm and an absorption cross-section
149 value of $1.13 \times 10^{-17} \text{ cm}^{-2}$ (see Daumont et al., 1992).⁴² We were working in large excess of O_3
150 compared to the organic monolayer, and $[\text{O}_3]$ remained approximately constant during the reaction.
151

2.2 Neutron Reflectometry (NR)

Our Neutron Reflectometry (NR) methodology was described elsewhere.⁴⁰ In short, specular NR
experiments were conducted using the white beam INTER reflectometer at the Rutherford Appleton
Laboratory in Oxfordshire, UK, employing neutron wavelengths ranging from 2.0 to 17.0 Å. The
reflected intensity was recorded at an incident angle of 0.8° , with a non-polarising supermirror
positioned at 0.75° , as a function of the momentum transfer, $q = (4\pi\sin\theta)/\lambda$, where λ represents the
wavelength and θ denotes the incident angle. The data were collected with a resolution ($\Delta q/q$) of 7%,
covering a total illuminated length of 165 mm. To minimize meniscus effects, the beam width was
adjusted to 50 mm. Time-resolved measurements were performed over intervals ranging from
minutes to several hours, with a time resolution of 20 seconds.

Neutron reflectivity (the 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 scattering
length density, SLD (ρ) and thickness (τ) of the monolayer as shown in equation (1) (based on Lu et
al., 2000):⁴³

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

The SLD and layer thickness can be inferred from the relationship between reflectivity and
momentum transfer measured by the instrument. The two parameters are fitted over the whole Q
range as a combined $\rho\tau$ value, which corresponds to a surface concentration of scattering length, from
which the surface concentration of the surfactant of interest can be determined if the scattering length
is known (e.g. $b = 315 \text{ fm}$ for deuterated oleic acid). Reflectivity curves of R vs. Q were fitted using
MOTOFIT⁴⁴ to give $\rho\tau$ values for each 20 s time slice. These fitted $\rho\tau$ values can be converted into
surface concentration (Γ) values for the surfactant following equation (2):⁴³

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

The error bars for the SLD \times thickness product were propagated using the calculated fitting errors for
each parameter obtained from MOTOFIT.⁴⁴ In order to achieve a sufficient contrast of the monolayer
compared to the other phases in the experimental system, a deuterated form of oleic acid (d -OA), was
used (Sigma-Aldrich at 98 % atom D; 99.9 %). 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 $\rho\tau$ values. For custom-
deuterated linoleic acid (d -LOA), the equivalent consideration leads to the presence of 31 deuterium
atoms in the fully deuterated LOA.



2.3 Multilayer-Py Modelling

Following the initial, basic kinetic analysis presented first, we also modelled the experimental data using the Multilayer-Py framework⁴⁵ in order to gain further mechanistic insights. Multilayer-Py⁴⁵ provides a framework for constructing kinetic multi-layer models, so that the model code is produced automatically for the user, removing potential human error in typing out the model code. This code is written in a readable format, enabling the code to be shared easily and facilitating more reproducible modelling results. This is further supported through the Jupyter notebook,⁴⁶ which is a document that incorporates both Python code and markdown text and is becoming an increasingly popular way of sharing and describing scientific code. The usefulness of Multilayer-Py has been demonstrated by application to the ozonolysis of OA⁴⁵ employing both KM-SUB⁴⁷ and KM-GAP⁴⁸ modelling approaches.

A detailed description of the KM-SUB model concept used in the present study has been presented previously⁴⁷ and is not repeated here. Essentially, the model splits our experimental system into a number of layers. The diffusion of reactants between each layer and the reaction of each component within each layer are resolved. Surface chemistry and the adsorption and desorption of gaseous species are also resolved. For this specific study, we introduced four different treatments of the oxidation of LOA by ozone: **(i)** single step oxidation considering the gradual build-up of ozone in our reaction chamber; **(ii)** the same assumptions as in (i), but now also assuming an inert residue remaining; **(iii)** two-step oxidation with a reaction product reacting with the reactant fatty acid in the second step; and **(iv)** the same assumptions as in (iii), but now also assuming an inert residue remaining at the interface.

3. Results and Discussion

In this section, experimental work is presented first followed by basic kinetic analysis and subsequently multi-layer modelling analysis is presented.

3.1 Oleic Acid Ozonolysis in Presence of Co-surfactant Linoleic Acid

We first studied two-component monolayers containing deuterated oleic acid (*d*-OA) and linoleic acid (*h*-LOA) to establish the possible impact of the linoleic acid co-deposition on the well-established reactivity of oleic acid towards ozone.^{e.g.32,33,36} Figures 2 (a) and (b) show the ozonolysis of a *d*-OA/*h*-LOA monolayer at a variety of ozone concentrations at room temperature and 3 ± 1 °C, respectively. Figure 2 (c) shows ozonolysis under the two temperature conditions overlaid, displaying only the highest and lowest ozone concentrations for visual clarity. These figures illustrate clearly that the change in temperature did not notably affect the rate of reaction.



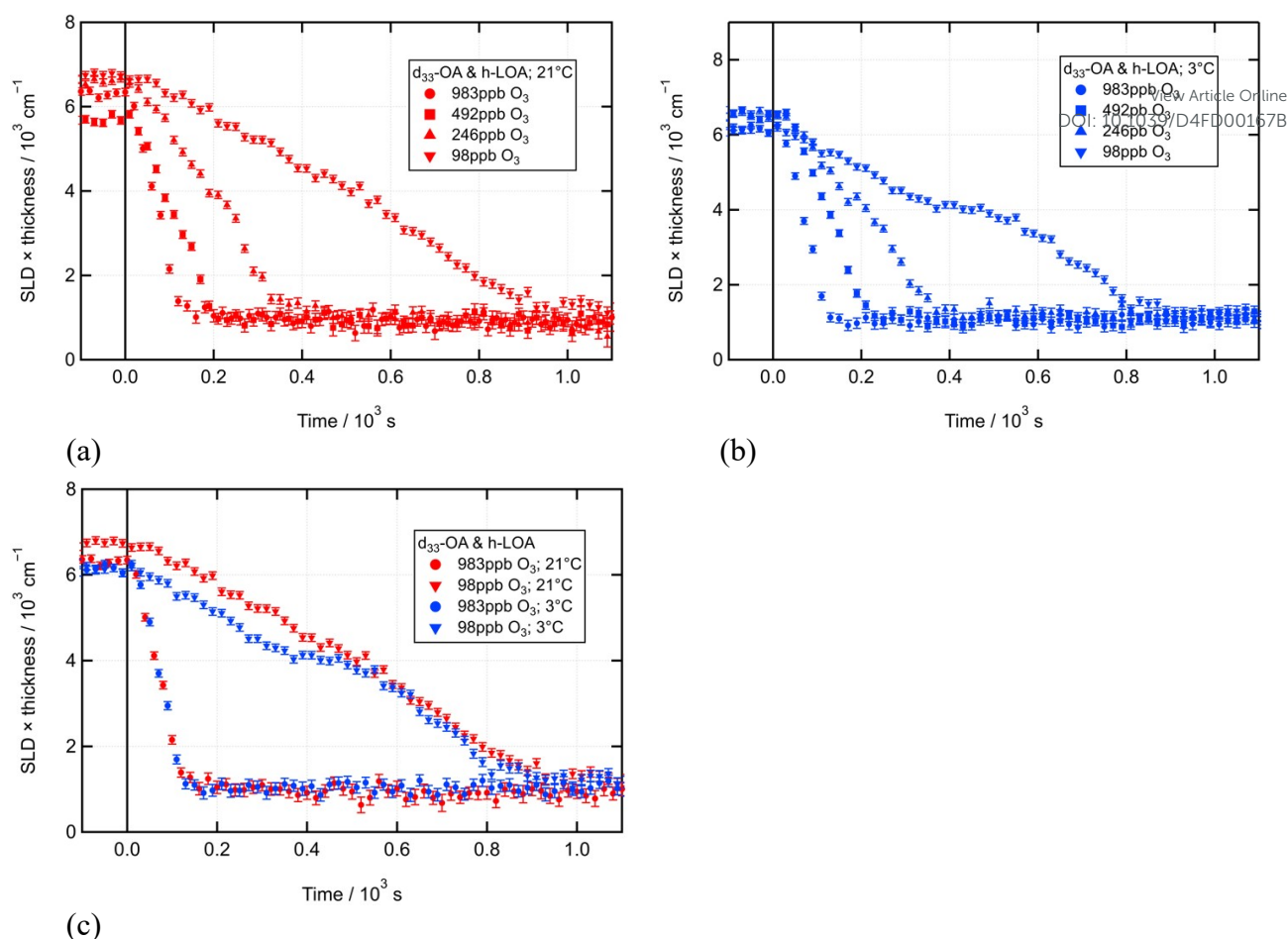


Figure 2 – Time evolution of fitted neutron reflectometry signal during oxidation of *d*-OA in a mixed monolayer with *h*-LOA (21 μ L of 0.81 g L⁻¹ *d*-OA/0.59 g L⁻¹ *h*-LOA; O₃ introduced at $t = 0$ s at various [O₃]) at (a) room temperature (21 \pm 1 $^{\circ}$ C) and (b) near-freezing (3 \pm 1 $^{\circ}$ C). Figure (c) re-plots the data for the highest and lowest ozone concentrations to compare directly the behaviour at the two different temperatures.

33 Pseudo-first-order rate coefficients were fitted to these neutron reflectometry time series displayed in
 34 Fig. 2 using the stretched exponential analytical model outlined in the Supplement Section S3 in
 35 Woden et al. (2021).³³ Fig. 3 displays a second order plot for this reaction (omitting data from the
 36 highest ozone concentration, as these reaction conditions were judged to be too fast to be fitted, given
 237 the limitation of a 20-second time resolution in our experimental approach). The second order
 238 rate coefficient obtained from these data is $2.0 \pm 0.4 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$. This is slightly lower than the values
 239 we measured for pure OA ($(2.2 \pm 0.4) \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ at 21 \pm 1 $^{\circ}$ C and $(2.2 \pm 0.2) \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ at
 240 2 \pm 1 $^{\circ}$ C),³³ but the error bars overlap significantly.

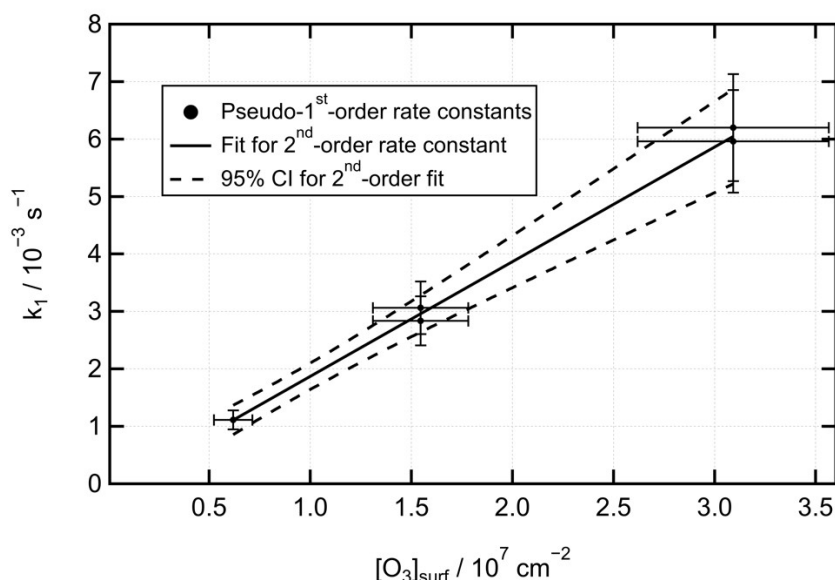
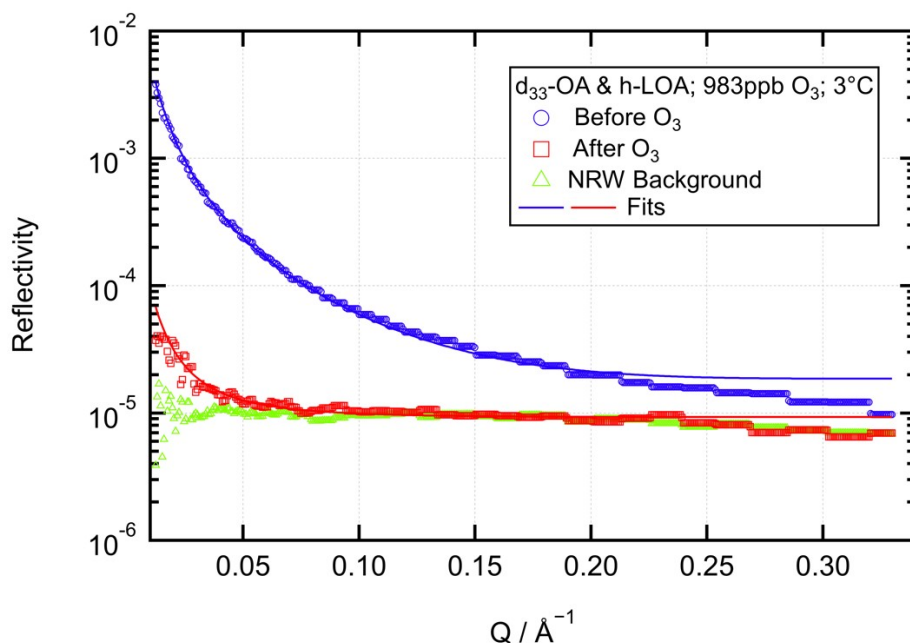


Figure 3 – Second order rate plot for the oxidation of *d*-OA in a mixed monolayer with *h*-LOA based on the data displayed in Fig. 2 (omitting the data for $[O_3] = 983$ ppb).

241 A further experiment was performed collecting neutrons over the full Q range accessible to INTER,
 242 in order to quantify any residue left behind after ozonolysis (as we have reported for low temperature
 243 ozonolysis of a pure OA monolayer; see Woden et al., 2021).³³ Figure 4 shows reflectivity curves
 244 before and after oxidation at 3 ± 1 °C where a residue can clearly be identified. Fitting monolayer
 245 parameters to these reflectivity curves to quantify the absolute amount of deuterated material
 246 adsorbed at the interface determined that 13 % of material present before ozonolysis remained
 247 afterward. This is similar to the range seen for pure OA monolayers at these temperatures (up to 11.1
 248 % deuterated residue was reported in Woden et al., 2021).³³ Fig. 4 shows that the fit to data collected
 249 before reaction deviates at high Q values. This is because the reflectivity background is not always
 250 Q -independent, as assumed in the MOTOFIT model and this becomes important at high Q where
 251 there is little signal compared to the background. This can be avoided by using a fixed background
 252 parameter derived from a clean air–NRW measurement, and this is the procedure used for fitting most
 53 of the data presented. This does, however, assume that the background will not change across the
 54 conditions studied (including temperature variations). Therefore, when carrying out experiments
 55 specifically to quantify post-oxidation residue under various conditions, in which distinguishing
 56 genuine residue from background signal is particularly important, this fixed-background method was
 57 avoided.



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Figure 4 – R vs. Q reflectivity plots before and after ozonolysis of d -OA in a mixed monolayer with h -LOA (21 μL of 0.81 g L^{-1} d -OA/0.59 g L^{-1} h -LOA; $[\text{O}_3] = 983 \pm 150$ ppb; 3 ± 1 $^\circ\text{C}$); null-reflecting water (NRW) background is shown for comparison.

Due to time constraints during neutron beamtime, no analogous experiment could be performed at room temperature. However, the kinetic data shown in Figures 2 (a) and (c) –collected across a restricted Q range and therefore not suitable for precise absolute quantification of small amounts of material– suggests that a similar residual monolayer remained.

3.2 Linoleic Acid Oxidation by Ozone

The primary focus of the experiments reported here was the study of the oxidation of linoleic acid (which can be achieved via ozonolysis or ozone-initiated autoxidation) as a monolayer at the air–water interface, and the effects of temperature and co-deposited film components on that oxidation process. To this end, pure d -LOA monolayers and mixed monolayers containing either h -OA or h -MO were oxidised under a variety of ozone concentrations at room temperature (21 ± 1 $^\circ\text{C}$) and at 3 ± 1 $^\circ\text{C}$. Figures 5–7 display the time series of the neutron reflectometry data for these reactions.

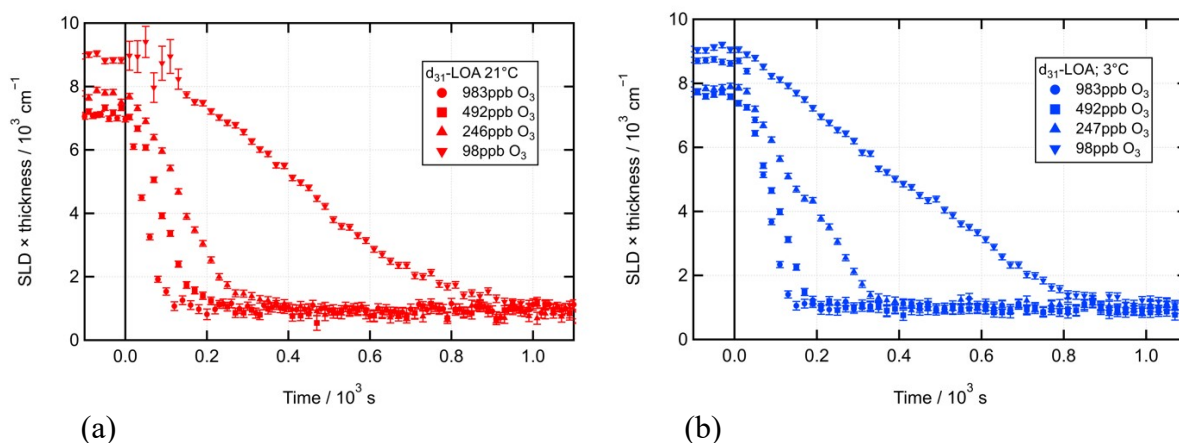
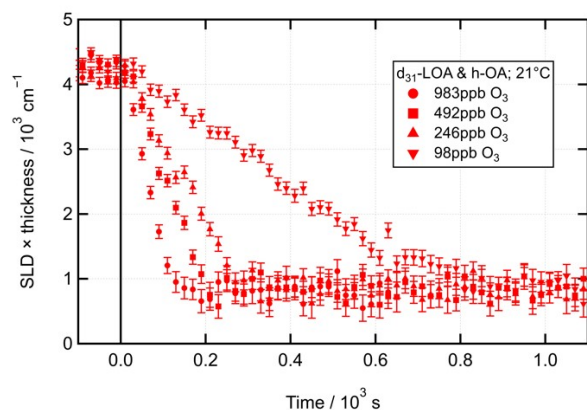


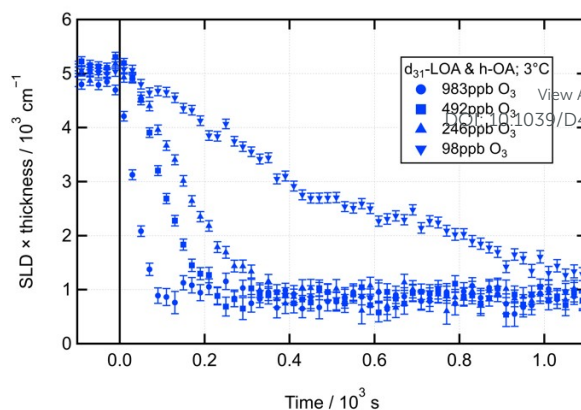
Figure 5 – Time series of neutron reflectometry data for the oxidation of pure d -LOA monolayers (21 μL of 1.4 g L^{-1} d -LOA; O_3 introduced at $t = 0$ s at various $[\text{O}_3]$) at (a) room temperature (21 ± 1 $^\circ\text{C}$) and (b) near freezing (3 ± 1 $^\circ\text{C}$).



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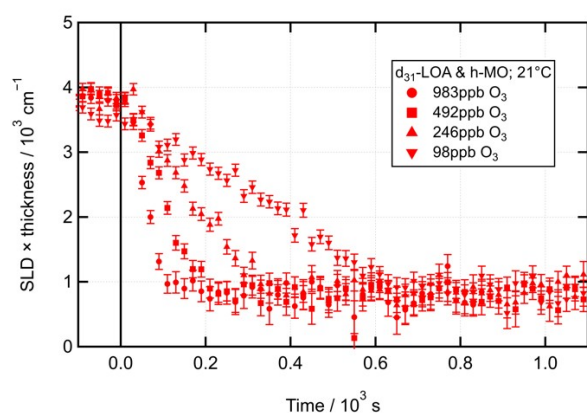


(a)

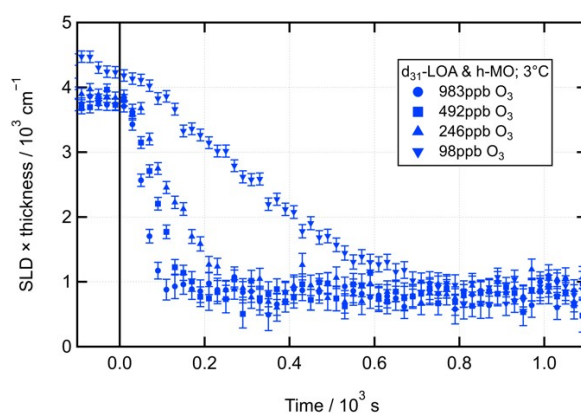


(b)

Figure 6 – Time series of neutron reflectometry data for the oxidation of a mixed monolayer of *d*-LOA with *h*-OA (21 μ L of 0.68 g L⁻¹ *d*-LOA/0.75 g L⁻¹ *h*-OA; O₃ introduced at $t = 0$ s at various [O₃]) at (a) room temperature (21 \pm 1 $^{\circ}$ C) and (b) near freezing (3 \pm 1 $^{\circ}$ C).



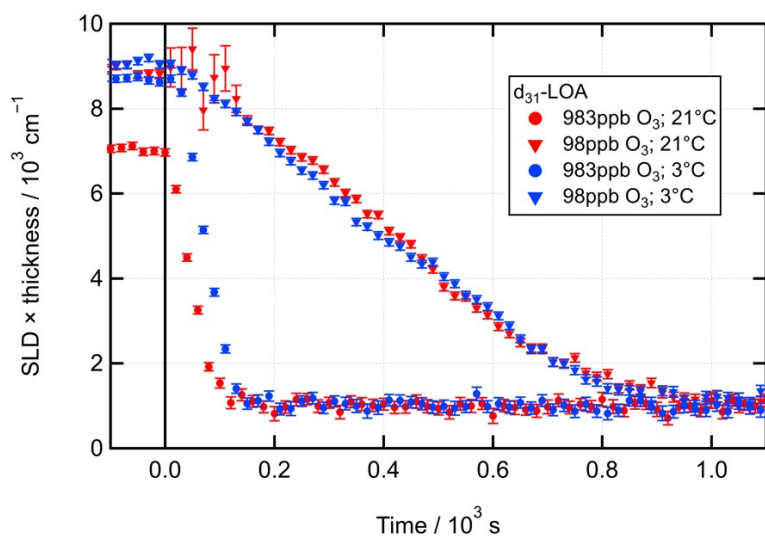
(a)



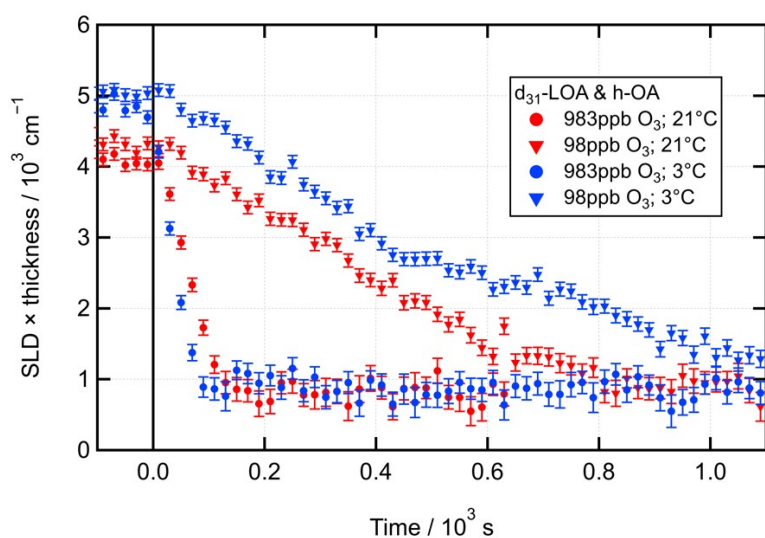
(b)

Figure 7 – Time series of neutron reflectometry data for the oxidation of a mixed monolayer of *d*-LOA with *h*-MO (21 μ L of 0.65 g L⁻¹ *d*-LOA/1.0 g L⁻¹ *h*-MO; O₃ introduced at $t = 0$ s at various [O₃]) at (a) room temperature (21 \pm 1 $^{\circ}$ C) and (b) near freezing (3 \pm 1 $^{\circ}$ C).

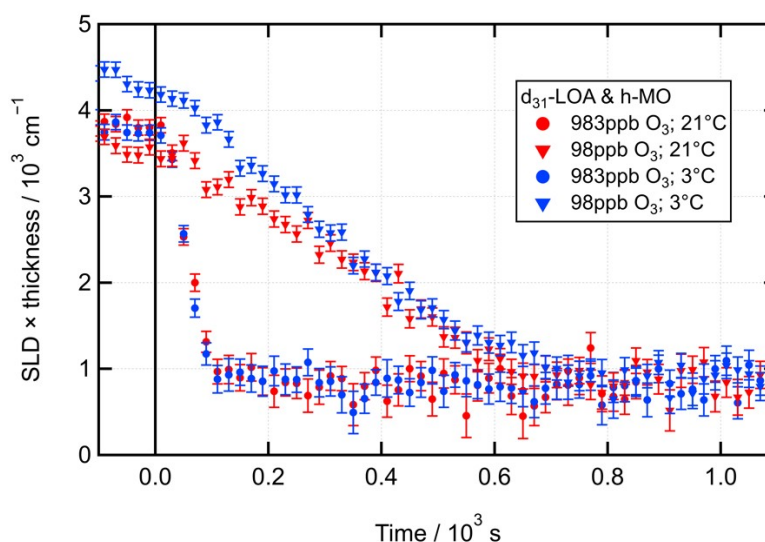
Figures 8 (a) to (c) overlay the temperature conditions, displaying only the highest and lowest ozone concentrations for visual clarity.



(a)



(b)

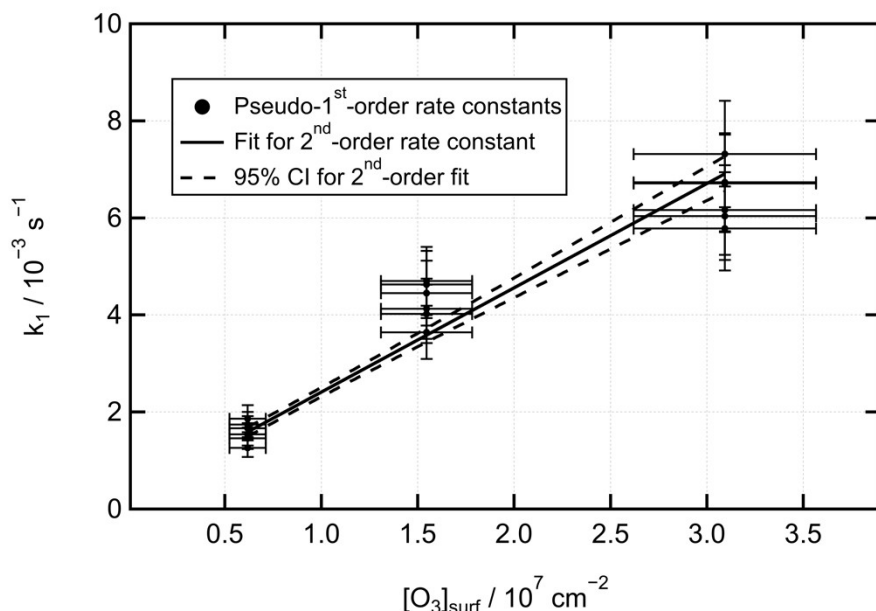


(c)

Figure 8 – Time series of neutron reflectometry data contrasting the two temperature conditions for the highest and lowest $[O_3]$ for the oxidation (see Figs 5–7 for individual plots for all $[O_3]$ studied) of (a) a pure d -LOA monolayer; (b) a mixed monolayer of d -LOA with h -OA; and (c) a mixed monolayer of d -LOA with h -MO.



281 Figure 9 displays a second-order plot for the LOA oxidation, and Table 1 summarises the fitted
 282 second-order rate coefficients for the three monolayer types in the two temperature conditions, as
 283 well as the rate coefficients for each monolayer type (treating temperature as irrelevant), for each
 284 temperature (treating monolayer type as irrelevant), and for all data combined. Table 1 demonstrates
 285 that neither the change in temperature nor the introduction of a co-deposited film component
 286 alongside *d*-LOA consistently affected the rate of reaction of LOA with ozone.



287 **Figure 9** – Second-order rate plot for the data displayed in Figures 5–8.

Table 1 – Second-order rate coefficients for *d*-LOA alone and in two mixed monolayer systems for two temperatures. Combined rate coefficients for each temperature (combining all mixture configurations), each mixture (combining both temperature conditions) and all data are also shown (95% confidence intervals are included as \pm values; confidence intervals are estimated for individual mixture/temperature pairs; confidence intervals are calculated statistically for all combined conditions).

Monolayer	Rate Coefficient / $10^{-10} \text{ cm}^2 \text{ s}^{-1}$		
	21 \pm 1 $^{\circ}\text{C}$	3 \pm 1 $^{\circ}\text{C}$	Combined
<i>d</i> -LOA	2.1 \pm 0.7	2.0 \pm 0.7	2.0 \pm 0.4
<i>d</i> -LOA/ <i>h</i> -OA	2.0 \pm 0.7	2.5 \pm 0.7	2.3 \pm 0.4
<i>d</i> -LOA/ <i>h</i> -MO	1.9 \pm 0.7	2.5 \pm 0.7	2.0 \pm 0.4
Combined Data	2.0 \pm 0.2	2.3 \pm 0.3	2.1 \pm 0.2

288 The rates displayed in Table 1 are higher compared to those reported by He *et al.*³⁹ However, our
 289 study uses a very different morphology (monolayer at the air–water interface) compared to that used
 290 by He *et al.* Furthermore, He *et al.* use much higher ozone concentration than our study (ca. 10 ppm
 291 compared to ca. 100 to 1000 ppb in the present study) and Chu *et al.* have specifically warned that,
 292 due to the competing mechanisms for this reaction that dominate under different conditions,
 293 extrapolating from high ozone concentrations downwards is likely to be problematic.³⁷ Other studies
 294 on this heterogenous reaction have mostly reported uptake coefficients, rather than rate coefficients,
 295 and these have varied by around an order of magnitude as reviewed by He *et al.*³⁹ The use of an
 296 uptake coefficient, which is more dependent on reaction conditions and geometry than is a rate
 297 coefficient, makes these studies less useful as a guide for what to expect in our study, which uses a
 298 monolayer at the air–water interface rather than particulate phase or film-coated flow tube setups.
 299 Differences in mechanism may also be driving some of these discrepancies.
 300

301 An experiment analogous to that described earlier for the d -OA/ h -LOA system (compare Fig. 4) was
 302 performed in order to quantify any post-oxidation residue. Again, only the low temperature was
 303 studied due to time constraints at neutron beamtime experiments. Figures 10 (a)–(c) display
 304 reflectivity curves before and after oxidation at 3 ± 1 °C for d -LOA, d -LOA/ h -OA and d -LOA/ h -MO,
 305 respectively.

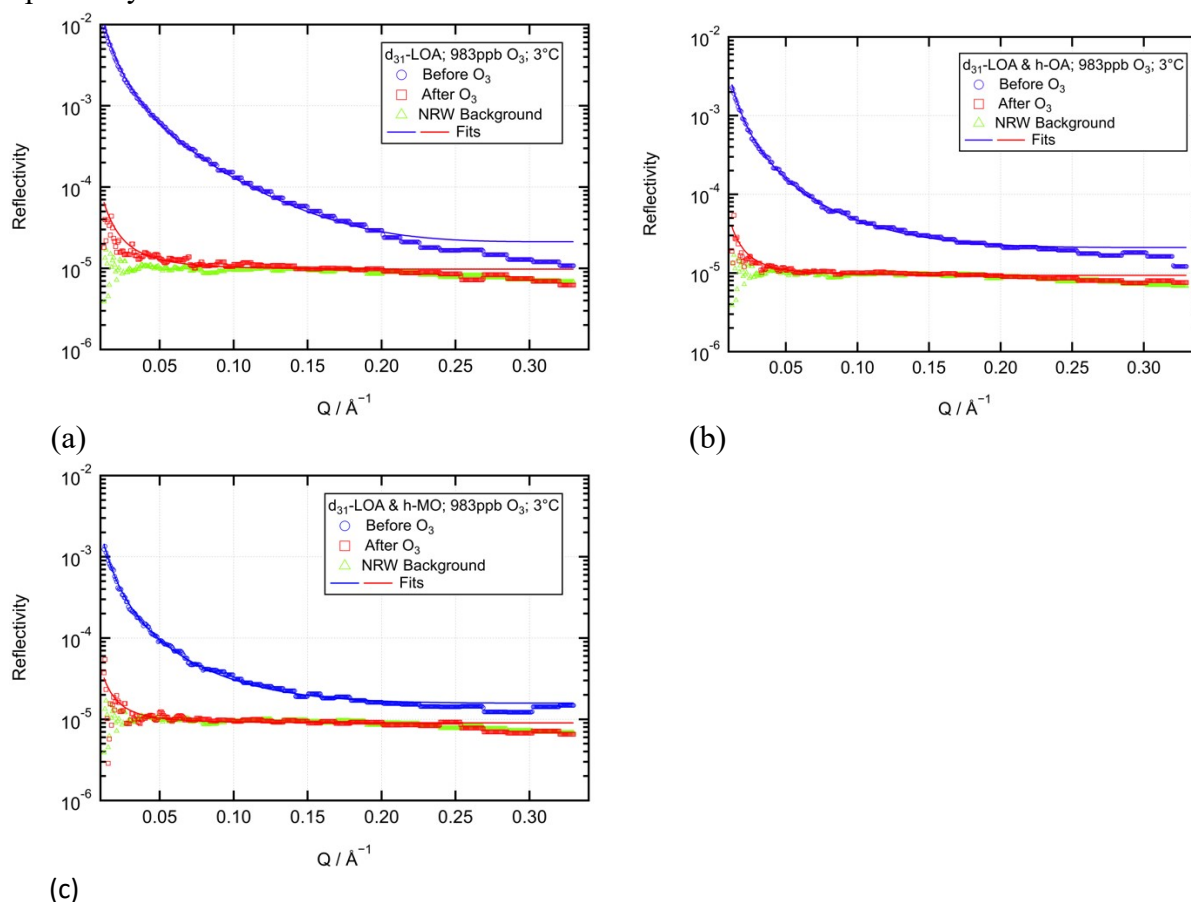


Figure 10 – R vs. Q reflectivity plots before and after reaction with O₃ of (a) a pure d -LOA monolayer (21 μ L of 1.4 g L⁻¹ d -LOA; [O₃] = 983 \pm 150 ppb; 3 \pm 1 °C); (b) d -LOA in a mixed monolayer with h -OA (21 μ L of 0.68 g L⁻¹ d -LOA/0.75 g L⁻¹ h -OA; [O₃] = 983 \pm 150 ppb; 3 \pm 1 °C); and (c) d -LOA in a mixed monolayer with h -MO (21 μ L of 0.65 g L⁻¹ d -LOA/1.0 g L⁻¹ h -MO; [O₃] = 983 \pm 150 ppb; 3 \pm 1 °C). Null-reflecting water (NRW) backgrounds are shown for comparison.

306 For d -LOA as a pure monolayer (Fig. 10 (a)), a residue is clearly observed, and fitting monolayer
 307 parameters quantifies this as ca. 7 % of the initial adsorbed deuterated material. For d -LOA in a mixed
 308 monolayer with h -OA, a residue is also observed and quantified as ca. 11 % of the initial adsorbed
 309 deuterated material. The data for d -LOA in a mixed monolayer with h -MO are slightly more difficult
 310 to interpret. The fitting process used throughout this work does successfully converge and fit a curve
 311 (displayed in Fig. 10 (c) as the red line) that would represent ca. 13 % of the initial adsorbed
 312 deuterated material. However, a visual appraisal of Fig. 10 (c) suggests that the post-oxidation
 313 reflectivity curve differs mainly from the null-reflecting water background in that it is unusually noisy
 314 at very low Q . From these noisy data alone it is very difficult to quantify the amount of residual
 315 monolayer, so further experimental confirmation would be useful. As well as repeating the low
 316 temperature residue quantification experiment for d -LOA/ h -MO, future work on this system could
 317 perform analogous room temperature experiments. As for the OA ozonolysis in the presence of LOA
 318 discussed earlier, the kinetic data collected over a limited Q range (see Figures 5–8) suggests that
 319 similar residual monolayers are present, but a full Q range characterisation would be very useful to
 320 confirm this. As further experiments were not feasible within the limitations of time-constrained



321 beamline facility access, this was one of the key motivations for the more detailed modelling analysis
322 presented in section 3.4.

323 The mechanism for LOA oxidation is far more complex than that for OA oxidation; the former
324 involves multiple competing pathways of ozonolysis and ozone-initiated autoxidation that result in
325 different products. One mechanism or the other has previously been observed to dominate depending
326 on ozone concentration and relative humidity.³⁷ The linear increase in pseudo-first-order reaction rate
327 with increasing ozone concentration suggests that one dominant mechanism is being observed across
328 the range of ozone concentrations used in this work (ca. 100 to 1000 ppb). Chu *et al.* noted that higher
329 ozone concentrations (above 250 ppb) inhibited the build-up of autoxidation products, as did higher
330 relative humidity.³⁷ All our work is carried out with ozone dissolved in a stream of dry oxygen, so
331 the relative humidity will be very low. Based on the range of ozone concentrations we employed and
332 the low relative humidity in our system, based on this literature we would have expected to observe
333 mainly autoxidation except for the highest [O₃] conditions. The autoxidation mechanism is complex
334 and is not presented here as we were not conducting any product analysis to directly distinguish
335 reaction mechanism, but rather focussing on reaction kinetics and residue formation in two-
336 component monolayers at different temperatures (a detailed explanation of LOA autoxidation can be
337 found in Chu *et al.*).³⁷

338 Given the abundance of saturated surfactants in atmospheric aerosols, we also carried out exploratory
339 experiments to test the effect of co-deposited stearic acid (SA) – the saturated analogue to OA – on
340 the LOA monolayer oxidation. Figure 11 (a) displays the oxidation of a *d*-LOA/*h*-SA monolayers at
341 two ozone concentrations at the two temperatures of interest. While this data set was too limited to
342 reliably calculate a second-order rate coefficient, a visual appraisal of the data suggests that
343 temperature once again does not exert a significant effect on the reaction rate. As far as the effect of
344 SA on the reaction rate goes, however, this preliminary data suggest that there may be an impact.
345 Figure 11 (b) illustrates the room temperature data overlaid with the analogous data for *d*-LOA/*h*-OA
346 oxidation. It does appear that the reaction is faster in the presence of SA. Further work would be
347 useful to establish whether this effect is reproducible, as there may be a degree of inter-run variability.
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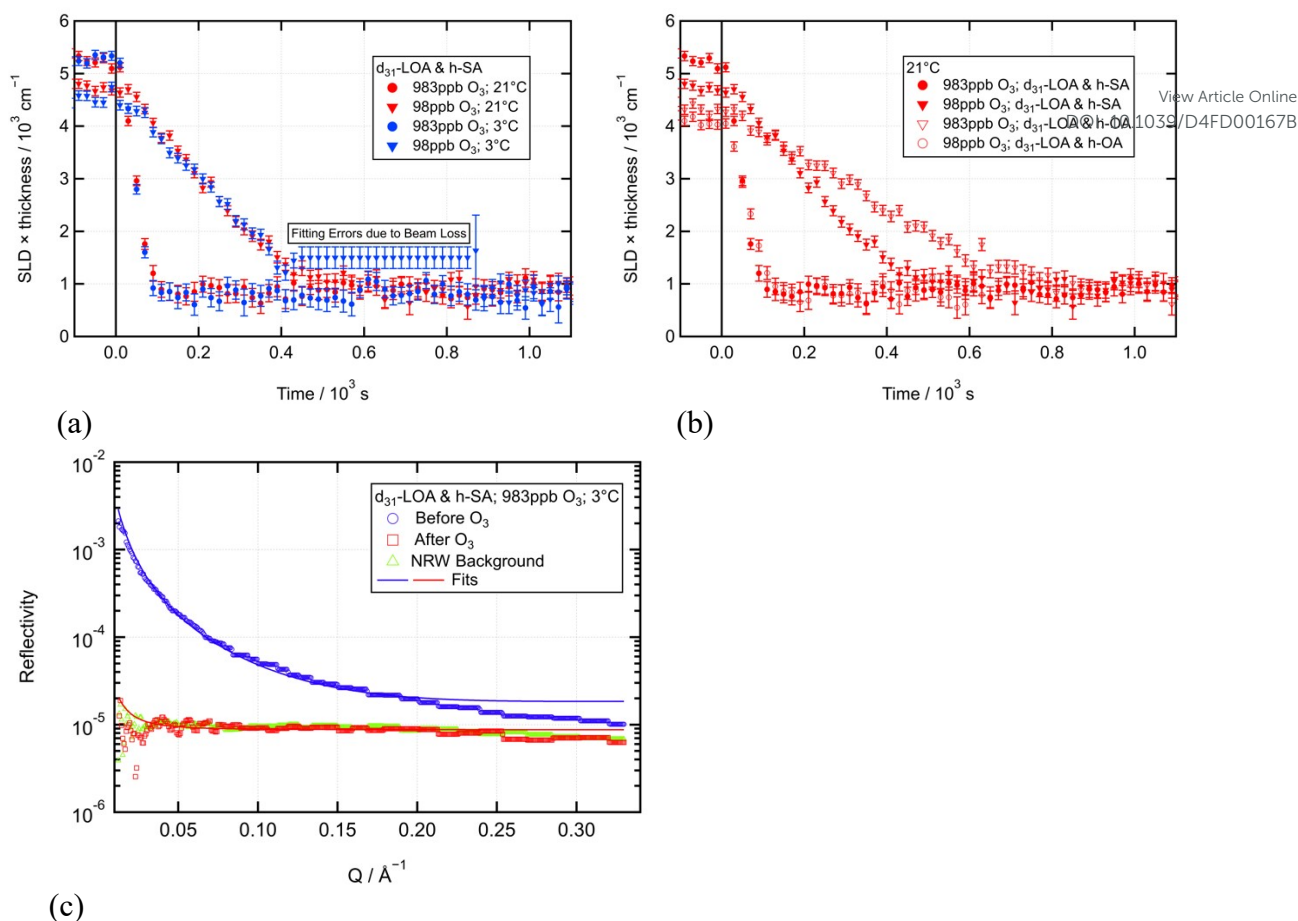


Figure 11 – (a) Time series of NR data contrasting the two temperature conditions for the highest and lowest [O₃] for the oxidation of *d*-LOA in a mixed monolayer with *h*-SA (21 μL of 0.65 g L⁻¹ *d*-LOA/0.80 g L⁻¹ *h*-SA; O₃ introduced at *t* = 0 s ; (b) time series of neutron reflectometry data contrasting the highest and lowest [O₃] for the oxidation of *d*-LOA at room temperature in mixed monolayers with *h*-SA and *h*-OA (21 μL of 0.68 g L⁻¹ *d*-LOA/0.75 g L⁻¹ *h*-OA or 0.65 g L⁻¹ *d*-LOA/0.80 g L⁻¹ *h*-SA; O₃ introduced at *t* = 0 s at two [O₃]); and (c) *R* vs. *Q* reflectivity plots before and after reaction with ozone of *d*-LOA in a mixed monolayer with *h*-SA (21 μL of 0.65 g L⁻¹ *d*-LOA/0.80 g L⁻¹ *h*-SA; [O₃] = 983 ± 150 ppb; 3 ± 1 °C; air-NRW background is shown for comparison).

A full *Q* range residue quantification experiment was performed for the *d*-LOA/*h*-SA system at 3 ± 1 °C, and the results are shown in Figure 11 (c). The post-oxidation reflectivity appears no different from the air-NRW background barring an intriguing oscillation at low *Q* that would merit further investigation as would the residue behaviour at 21 ± 1 °C.

3.3 Multilayer-Py Modelling Results

The Multilayer-Py framework⁴⁵ was used with the KM-SUB model⁴⁷ to gain further mechanistic insights. The model was run in four scenarios: (i) considering a single reaction process with initial ozone build-up modelled in the reaction chamber; (ii) additionally considering a residue remaining after reaction; (iii) additionally considering a secondary reaction step without residue; and (iv) considering the additional reaction step and residue formation. Model fits quickly demonstrated that both ozone build-up in the reaction chamber and residue formation need to be considered to obtain a reasonable fit, while one stage and two stage oxidation mechanisms resulted in very similar decay shapes. We thus focussed on the single-step oxidation with ozone build-up and residue formation to fit the entire experimental data set with a consistent set of assumptions with min. complexity.

383 Examples of the optimised model output are displayed in Figures 12–14 (the full set of model fits for
384 the different $[O_3]$ is provided in the Electronic Supplementary Information (ESI)).

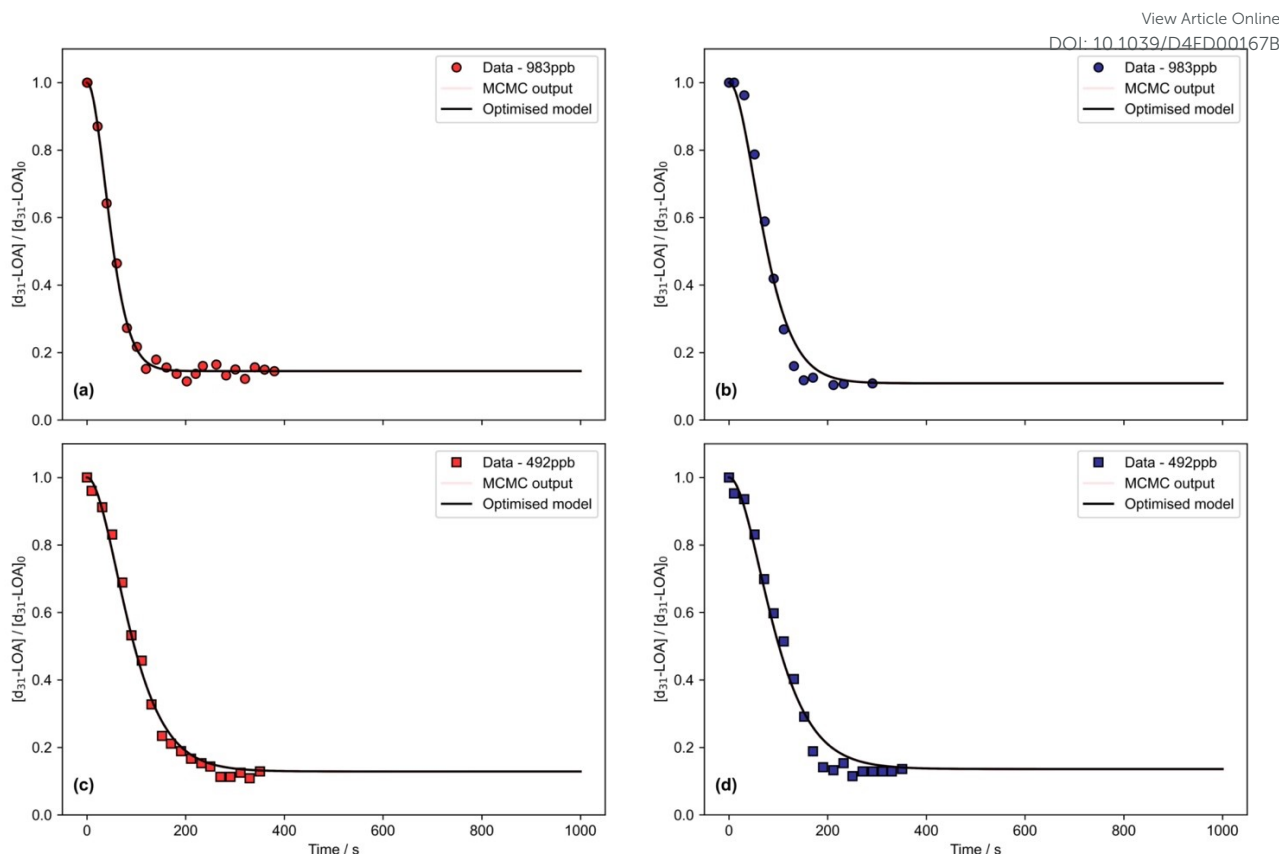


Figure 12 – Multilayer-Py⁴⁵ modelling fits to selected $[O_3]$ for pure *d*-LOA oxidation (fits to the full set of $[O_3]$ conditions is presented in the ESI; the model runs presented here consider ozone build-up in the reaction chamber, a single-stage oxidation process and residue formation). The figures display the normalised decay of *d*-LOA as a function of time with experimental data (red and blue symbols), the results of the global optimisation using Markov chain Monte Carlo (MCMC) sampling (pink lines close to the best fit) and the optimised model fit (solid black line). **(a)** 983 ppb & 21 ± 1 °C; **(b)** 983 ppb & 3 ± 1 °C; **(c)** 492 ppb & 21 ± 1 °C; and **(d)** 492 ppb & 3 ± 1 °C.

The kinetic multi-layer modelling demonstrated that model optimisation using Markov chain Monte Carlo (MCMC) sampling yields good fits for the rate coefficients obtained with standard kinetic fitting (see fits in Figs 12–14 which are using the rate coefficients stated in Table 1).



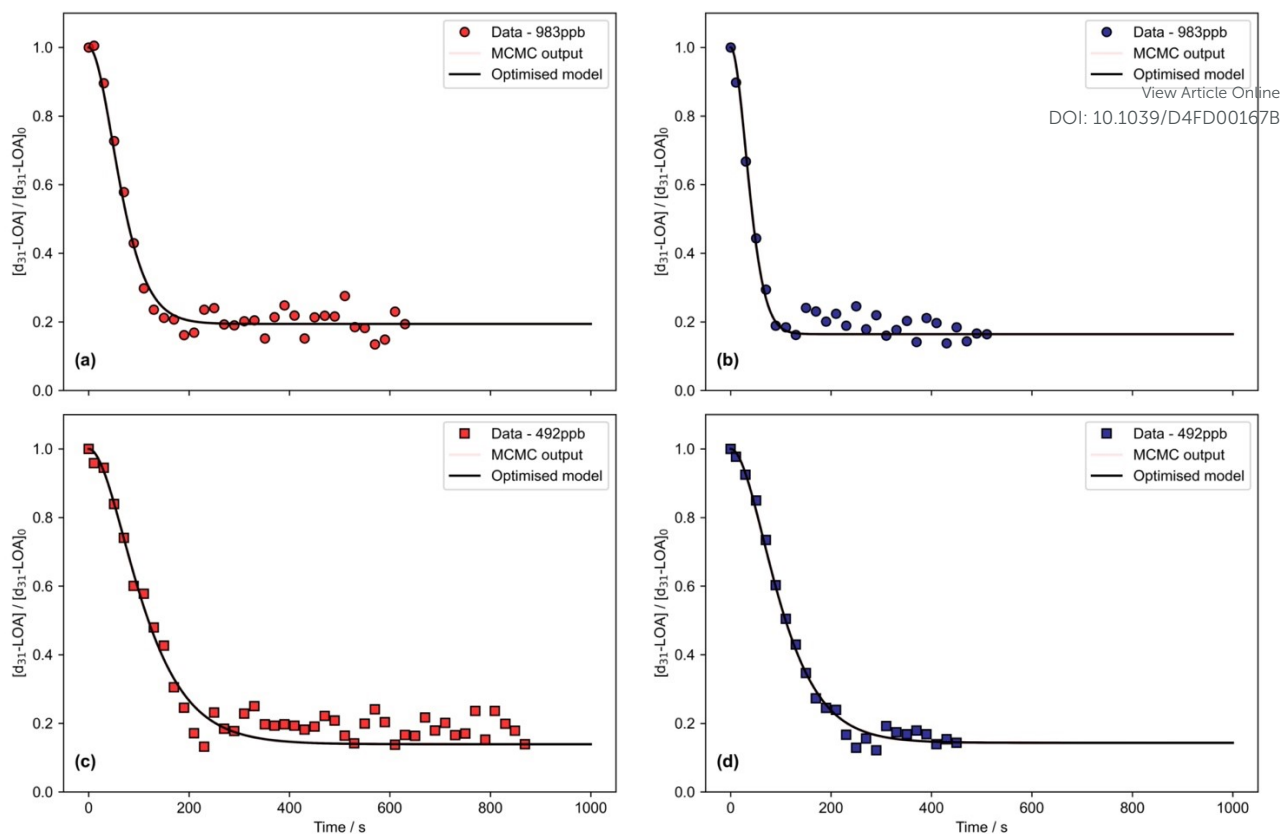
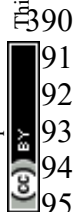


Figure 13 – Multilayer-Py⁴⁵ modelling fits to selected $[O_3]$ for d -LOA/ h -OA oxidation (fits to the full set of $[O_3]$ conditions is presented in the ESI; the model runs presented here consider ozone build-up in the reaction chamber, a single-stage oxidation process and residue formation). The figures display the normalised decay of d -LOA as a function of time with experimental data (red and blue symbols), the results of the global optimisation using Markov chain Monte Carlo (MCMC) sampling (pink lines close to the best fit) and the optimised model fit (solid black line). **(a)** 983 ppb & 21 ± 1 °C; **(b)** 983 ppb & 3 ± 1 °C; **(c)** 492 ppb & 21 ± 1 °C; and **(d)** 492 ppb & 3 ± 1 °C.

Furthermore, Multilayer-Py allowed optimised residue fitting. The results (see Table 2) suggest that the residues for pure d -LOA (Fig. 12) are consistently lower (11 – 14%) than for its mixtures with h -OA (13 – 27%; Fig. 13) followed by the mixtures with h -MO (19 – 27%; Fig. 14). The modelling showed no significant difference between residues at the two different temperatures: only for the d -LOA/ h -MO mixtures (see Table 2) did we find a small difference with the residue averaging at ca. 23% for 3 ± 1 °C compared to ca. 20% for 21 ± 1 °C, however no clear difference was observed for the other monolayer compositions.

Table 2 – Relative residue remaining after oxidation obtained through Multilayer-Py⁴⁵ model fitting for different $[O_3]$ and the two temperatures for the three different monolayers.

Monolayer	Relative residue / %							
	21°C & 983 ppb	21°C & 492 ppb	21°C & 246 ppb	21°C & 98 ppb	3°C & 983 ppb	3°C & 492 ppb	3°C & 246 ppb	3°C & 98 ppb
d -LOA	14.48	12.86	14.31	12.07	10.87	13.59	12.39	13.17
d -LOA/ h -OA	19.38	13.90	16.22	20.21	16.40	14.31	12.80	26.79
d -LOA/ h -MO	21.32	19.14	20.68	19.94	22.49	19.76	22.94	27.39

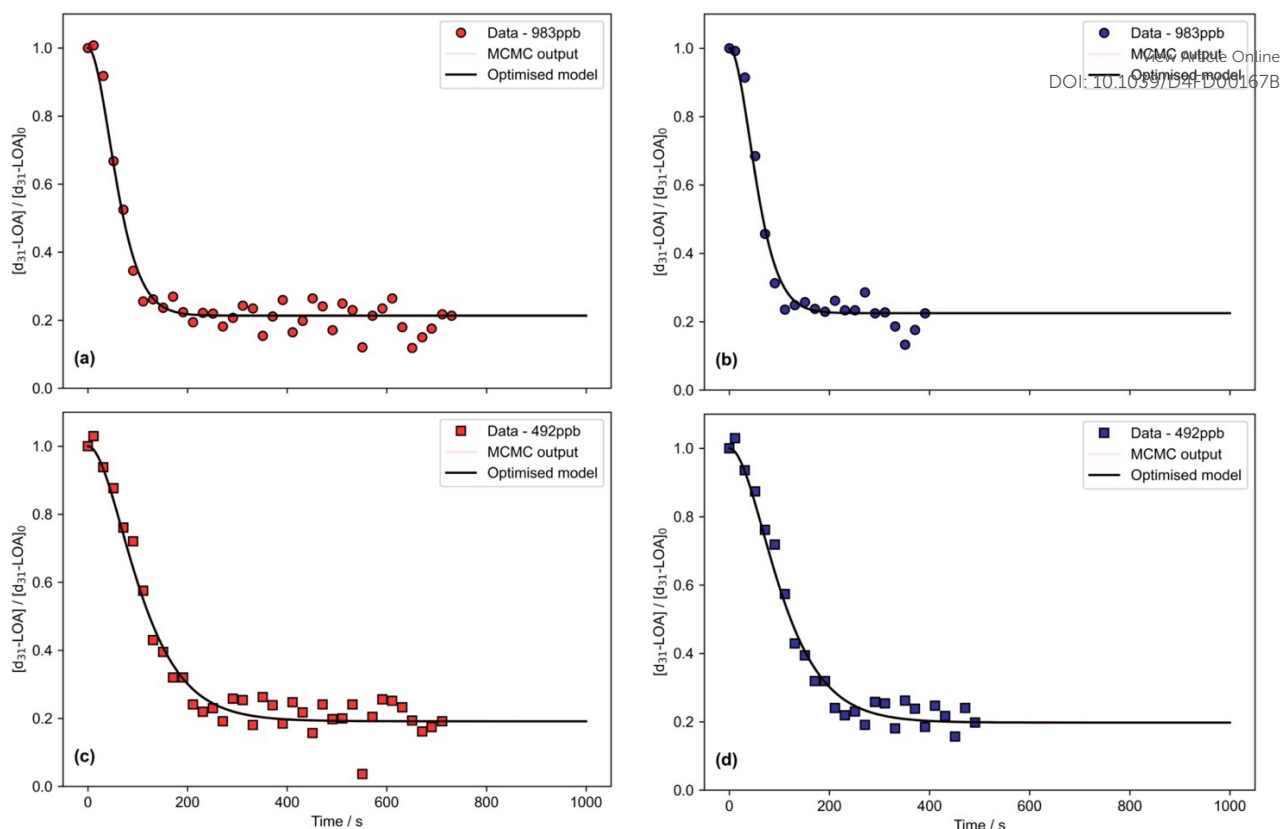


Figure 14 – Multilayer-Py⁴⁵ modelling fits to selected $[O_3]$ for d -LOA/ h -MO oxidation (fits to the full set of $[O_3]$ conditions is presented in the ESI; the model runs presented here consider ozone build-up in the reaction chamber, a single-stage oxidation process and residue formation). The figures display the normalised decay of d -LOA as a function of time with experimental data (red and blue symbols), the results of the global optimisation using Markov chain Monte Carlo (MCMC) sampling (pink lines close to the best fit) and the optimised model fit (solid black line). (a) 983 ppb & 21 ± 1 °C; (b) 983 ppb & 3 ± 1 °C; (c) 492 ppb & 21 ± 1 °C; and (d) 492 ppb & 3 ± 1 °C.

Overall, the modelling at room temperature results in slightly better fits across the different monolayer compositions at all $[O_3]$ except for the lowest concentration of 98 ppb (see Fig. S25 in the ESI). For pure d -LOA at low $[O_3]$ (98 ppb) the decay shape consistently deviates from that compatible with a single decay process (see Figs S25(a) & (b)); this deviation is weaker, but still visible, for the mixtures with h -MO and less apparent for the h -OA mixtures (contrast Figs S25(c) & (d) to Figs S25(a) & (b)); the data were too limited to quantify this effect, but this observation is consistent with previous work suggesting that the additional process of autoxidation becomes important at low O_3 .³⁷

3.4 Effects of Low Temperatures

Overall, we found that the temperature change from 21 ± 1 to 3 ± 1 °C for the systems studied here did not affect the reaction rate, which is ranging from 1.9 to $2.5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and is thus similar to that of pure oleic acid ($2.2 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ both at 21 ± 1 and 2 ± 1 °C).³³ This lack of a measurable effect on the kinetics over the comparatively small temperature range accessible in our system is consistent with our previous work – temperatures are likely to play a more important role for the kinetics when phase boundaries are crossed, which would warrant further study.

Kinetic multi-layer modelling using our Multilayer-Py package allowed us to optimise the residue fitting as residue formation showed a temperature dependence in our previous work for oleic acid

420 ozonolysis (Woden et al., 2021).³³ While the modelling results presented here suggest that the
421 residues for pure *d*-LOA are consistently lower (11 – 14%) than for its mixtures with *h*-OA (13 –
422 27%) and *h*-MO (19 – 27%), it showed no clear difference between residues at the two different
423 temperatures: only for the *d*-LOA/*h*-MO mixtures did we find a small difference with the residue
424 averaging at ca. 23% for 3 ± 1 °C compared to ca. 20% for 21 ± 1 °C, but no significant difference
425 was observed for the other monolayer compositions across the different O₃ levels.

426 Since the low-temperature conditions used here are atmospherically realistic, it is key to understand
427 if a product film persists and thus needs to be considered when assessing the impact of unsaturated
428 fatty acid partitioned to the air–water interface. The presence of stable (non-oxidisable) reaction
429 products could also lead to a build-up of inert monolayers during the aerosol life cycle with potential
430 implications for cloud formation. Our previous work on oleic acid ozonolysis³³ showed that a residual
431 surface film (likely formed of ozonolysis products nonanoic acid and a mixture of azelaic and 9-
432 oxononanoic acids) was retained at the interface after ozonolysis at low temperatures, but not at room
433 temperature. For the binary mixtures studied here, we did not find such a clear temperature
434 dependence of residue formation. As surfactants will be present in the atmosphere in complex, multi-
435 component mixtures, it is important to understand the reasons for these different behaviours even for
436 closely related systems. While the temperature change did not impact on the kinetics, residue
437 formation may be affected, thus altering the persistence of the organic character at the surface of
438 aqueous droplets.

439 3.5 Future Work

440 As LOA, OA, and MO are all closely related, unsaturated fatty acids (a fatty acid methyl ester in the
441 case of MO) with broadly similar physical properties, it is likely that they mix well at the interface,
442 and it is also likely that LOA and stearic acid (SA) mix poorly, as do OA and SA (see Skoda et al.,
443 2017).⁴⁰ Due to this similarity to systems already studied, offline characterisation (e.g. via Brewster
444 angle microscopy and Wilhelmy plate tensiometry) was not performed, but such investigations would
445 be useful, especially if less well understood atmospheric surfactants would be considered. Additional
446 work on the mixture with SA would allow to quantify the rate coefficient in this mixed monolayer
447 system which would be a very useful addition since the reaction appears to be faster in the presence
448 of SA based on our preliminary work, but this needs confirmation since there is a reasonable degree
449 of inter-run variability.

450 Furthermore, it would be very useful to explore further the kinetic behaviour at lower ozone
451 concentrations (as long as reactions can still be observed within the limited timeframe of neutron
452 beamtime experiments) given the unusual decay shapes we found especially for pure *d*-LOA at 98
453 ppb. This would also extend the range of data available for second-order fitting increasing the
454 robustness of the fitted parameters.

455 Finally, it would be worth to establish the residue remaining after reaction for a wider range of
456 conditions also including full *Q* range runs at room temperature.

458 4 Conclusions

459 Our experiments focussed on the oxidation of deuterated LOA (*d*-LOA) as a monolayer, and in mixed
460 two-component films with either oleic acid (*h*-OA) or its methyl ester, methyl oleate (*h*-MO), at two
461 temperatures using ozone levels of ca. 100 ppb to 1 ppm. We found that the temperature change did
462 not affect the reaction rate. We also measured the rate coefficient for *d*-OA/*h*-LOA mixed monolayers
463 to be $2.0 \pm 0.4 \times 10^{-10}$ cm² s⁻¹ and thus ca. 10% below that measured for pure *d*-OA earlier,³³ but the
464 uncertainties overlap significantly.

465 Kinetic multi-layer modelling was used to: (i) confirm the rate coefficients obtained with standard
466 kinetic fitting; (ii) illustrate that for pure *d*-LOA at low [O₃] (98 ppb) the decay shape consistently
467 deviates from that compatible with a single decay process; this deviation was found to be weaker, but
468



469 still visible, for the mixtures with *h*-MO and less apparent for the *h*-OA mixtures (this observation is
470 consistent with previous work suggesting that the additional process of autoxidation becomes
471 important at low O₃, but the reason for the differences between pure *d*-LOA and the two-component
472 mixtures merits further investigation); and (iii) optimise the residue fitting suggesting that the
473 residues for pure *d*-LOA are consistently lower (11 – 14%) than for its mixtures with *h*-OA (13 –
474 27%) followed by the mixtures with *h*-MO (19 – 27%). The latter trend in the model data is consistent
475 with full *Q* range NR experiments carried out at the highest [O₃] conditions, although these
476 experiments suggest a lower residue proportion ranging from ca. 7% to 13%.

477
478 In summary, neither the change in temperature nor the introduction of co-deposited film components
479 alongside *d*-LOA consistently affected the LOA oxidation rates, but the deviation from a single
480 process decay behaviour (indicative of autoxidation) at 98 ppb is clearest for pure *d*-LOA, weaker for
481 the *h*-MO mixtures and the weakest for *h*-OA mixtures.

482
483 As surfactants will be present in the atmosphere in complex, multi-component mixtures, it is
484 important to understand the reasons for these different behaviours even in two-component mixtures
485 of closely related species. The rates we found were fast compared to those reported earlier for a
486 different LOA morphology under much higher ozone concentrations. Our work demonstrates clearly
487 that it is essential to employ atmospherically realistic ozone levels as well as multi-component
488 mixtures especially to understand LOA behaviour at low O₃ in the atmosphere. While the temperature
489 change did not play a crucial role for the kinetics, residue formation may be affected, potentially
490 impacting on the persistence of the organic character at the surface of aqueous droplets with a wide
491 range of atmospheric implications.

492 493 Conflict of Interest

494 The authors confirm that there are no conflicts of interest to declare.

495 496 Data Availability

497 The modelling data supporting this article have been included in the Electronic Supplementary
498 Information (ESI). The underlying neutron reflectometry data is available at the ISIS Neutron &
499 Muon Source (<https://doi.org/10.5286/ISIS.E.RB1910615>) and the experimental work presented here
500 is also part of Chapter 7 of Ben Woden's PhD thesis which is available in the University of Reading's
501 repository (https://centaur.reading.ac.uk/96396/2/19011604_WODEN_Thesis.pdf).

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507 (<https://doi.org/10.5286/ISIS.E.RB1910615>).

508 509 Authors' Contributions

510 BW carried out the experimental work (jointly with MS, CP and AM) and wrote a thesis chapter for
511 his PhD at the University of Reading that formed the basis for this manuscript; CP was lead supervisor
512 for BW's PhD; CP wrote the abstract submitted for the *Faraday Discussions* and the first draft of this
513 manuscript; MS co-supervised BW's PhD project, supported the experimental work and data analysis
514 at ISIS and contributed substantially to data analysis and interpretation; YS carried out the Multilayer-
515 Py modelling analysis and created the modelling plots; AM contributed to the experiments and model
516 analysis; all co-authors contributed to the final paper.

517

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Data Availability

The modelling data supporting this article have been included in the Electronic Supplementary Information (ESI). The underlying neutron reflectometry data is available at the ISIS Neutron & Muon Source (<https://doi.org/10.5286/ISIS.E.RB1910615>) and the experimental work presented here is also part of Chapter 7 of Ben Woden's PhD thesis which is available in the University of Reading's repository (https://centaur.reading.ac.uk/96396/2/19011604_WODEN_Thesis.pdf).

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