Night-time oxidation at the air–water interface: cosurfactant effects in binary mixtures†

Federica Sebastiani, †ab Richard A. Campbell †b and Christian Pfrang †d*acd

The ageing of organic-coated aqueous aerosols at night is investigated by reacting NO₃ with binary surfactant mixtures floating on water. The surfactants are oleic acid (OA), methyl oleate (MO) and stearic acid (SA). Deuterated surfactants mixed with hydrogenous surfactants were studied using neutron reflectometry to determine the reaction kinetics of organic two-component monolayers with NO₃ at the air–water interface for the first time. We measured the rate coefficients for OA monolayers, mixed with hydrogenous co-surfactant MO or SA to be \((3 \pm 1) \times 10^{-8}\) cm² per molecule per s or \((3.6 \pm 0.9) \times 10^{-8}\) cm² per molecule per s and MO monolayers mixed with hydrogenous co-surfactant OA or SA to be \((0.7 \pm 0.4) \times 10^{-8}\) cm² per molecule per s or \((3 \pm 1) \times 10^{-8}\) cm² per molecule per s. The initial desorption lifetimes of NO₃, \(\tau_{\text{NO}_3}\), were 8 ± 3 ns, 14 ± 4 ns, 12 ± 3 ns and 21 ± 10 ns. The approximately doubled desorption lifetime for MO–SA compared to the other mixtures is consistent with a more accessible double bond associated with the larger area per molecule of MO in the presence of SA facilitating NO₃ attack. The significantly slower reactive loss of MO–OA compared to a MO monolayer demonstrates that multi-component surfactant mixtures need to be studied in addition to single-component monolayers. Such a retarded decay would cause the residence time to change from ca. 4 to 22 minutes associated with increased transport distances of surfactant species together with any other pollutants that may be protected underneath the surfactant film.

Environmental significance

The most significant result was a ca. six-fold slower decay for the MO–OA binary mixture compared to a MO monolayer demonstrating that matrix effects of cosurfactants affect reaction kinetics; data from monomolecular surfactant experiments thus cannot simply be added up to understand the decay of these species in complex atmospherically relevant mixtures. Such a retardation of oxidative decay was not found for binary mixtures of surfactants with carboxylic acid headgroups. It thus seems likely that the less stable species at the air–water interface are more strongly affected by co-surfactants. This is particularly important given these species may be more likely to be encountered in the atmosphere than those with perfectly hydrophilic headgroups that are most commonly studied in the laboratory.

1 Introduction

Atmospheric aerosols are of key importance because of their impact on Earth’s radiative balance and on cloud formation, but also due to their link to air pollution. These aerosols originate both from natural and man-made sources. Aerosol behaviour is strongly affected by the presence of organic material both in the bulk and at the surface. Organic components of atmospheric aerosols are often surface-active including organic acids and diacids, proteins and humic-like substances (HULIS). Key components of surface-active organic aerosols are fatty acids; it is important to note that phase behaviour especially for fatty acids is highly temperature dependent, and little data are available for temperatures lower than ambient e.g. ref. 15, which are particularly relevant for surfactants in clouds. Atmospheric fatty acids include saturated (such as palmitic acid) and unsaturated acids in particular oleic acid which is found both in marine and cooking aerosols. Cooking emissions have been proposed to contribute ca. 10% to the man-made emission of small particulate matter (PM₂.₅) at 320 mg per person per day based on measurements in London. The atmospheric lifetime of
aerosol particles is largely determined by chemical ageing initiated by the oxidants nitrate radicals (NO₃), hydroxyl radicals (OH) and ozone (O₃). For investigation of this chemical aerosol ageing, it is crucial to study the heterogeneous reactions occurring between the aerosol and these gas-phase oxidants. Homogeneous chemistry is relatively well understood at a molecular level, while the details of heterogeneous chemistry remain largely unknown. Field measurements suggest that heterogeneous reactions substantially affect the chemical composition of particles, in particular that of their surface films.\(^{24}\) Such reactions may alter key particle properties such as aerosol hydrophilicity, toxicity as well as their optical properties. For example, polycyclic aromatic hydrocarbons (PAHs) as well as phthalates have been identified together with oleic acid in marine aerosols\(^{25}\) with several studies suggesting that surface-active coatings on organic aerosols shield these PAHs, thus increasing their ability to be transported further and cause harm.\(^{26–28}\) The vast majority of studies to date have investigated the heterogeneous reactions of organic aerosols with O₃ and OH, which are the main oxidants during daytime. During nighttime, [OH] is very low while the concentration of the photo-labile NO₃ will build up, so that NO₃ becomes highly significant. Therefore, while OH controls the chemistry of the daytime atmosphere, NO₃ radicals have a similar role during the night.\(^{29–32}\) Khan and co-workers\(^{33}\) reported increases in NO₃ of up to 15 ppt from pre-industrial times to the present day.

In many cases heterogeneous reactions have been studied using organic droplets or thick films.\(^{34,35}\) However, it has been shown that experimental studies of organic molecules self-assembled at the surface of water rather than purely organic aerosols alone are key to understanding atmospheric ageing of aerosols covered in organic material.\(^{3,36}\)

In the work presented here organic monolayers at the air-water interface have been used as proxies for organic-coated aqueous atmospheric aerosols, and their reactions with NO₃ are studied. Most of the previous work with surfactant monolayers has focussed on ozonolysis,\(^{37–40}\) with much less studies focussing on reaction with nitrate radicals.\(^{41–43}\) Furthermore, the majority of the previous investigations has described the reaction of one surfactant with the oxidant, while it is increasingly clear that it is needed to include more than one surfactant species when mimicking the organic coated atmospheric aerosols.

The surfactant species chosen are oleic acid (OA), methyl oleate (MO) and stearic acid (SA). OA, OA\(^{34,37,38,41,44,45}\) MO\(^{26,29,41,42,46–49}\) and SA\(^{50}\) are popular model systems for atmospheric surfactants. MO, the methyl ester of OA, is a main component of biodiesel (chemical name: fatty acid methyl esters or ‘FAME’),\(^{51}\) likely leading to an increased atmospheric abundance in the future given up to 7% of FAME is added to standard petroleum diesel in the EU to reduce greenhouse gas emissions; higher proportions of FAME in petroleum diesel (10% FAME sold as ‘B10’ and 20% FAME sold as ‘B20’) and pure FAME (‘B100’) become increasingly common fuel alternatives across a number of European countries such as Germany, France and Finland.

This range of molecules allows the investigation of the effects of head group and degree of unsaturation on the reaction kinetics and products formed. Building on our previous work on single surfactants,\(^{44}\) we focussed this study on the impact of co-surfactants on the NO₃-initiated oxidation of these surfactants in binary mixtures.

What is lacking so far in the literature is the link between laboratory studies of single component surfactant films and real atmospheric surfactant materials. Key questions are if studies of single surfactants can be combined in modelling studies to describe more complex real surfactant compositions and also if co-surfactants will affect the loss of the reactive surfactant species. Xiao and Bertram\(^{45}\) investigated NO₃-initiated oxidation of binary mixtures containing the unsaturated organic MO and saturated molecules (diethyl sebacate, diocyl sebacate, and squalane) as matrix molecules. They have used a rotating-wall flow tube reactor coupled to a chemical ionization mass spectrometer (CIMS) with the aim to better understand the reactivity of unsaturated organics in multicomponent and multiphase atmospheric particles; their results suggest that for liquid binary mixtures the reactivity of methyl oleate depended on the matrix molecule. Our method of neutron reflectometry (NR) is particularly well suited for the study of these mixtures, since deuteration of one of the surfactants in the binary mixture

![Fig. 1](image-url)  
**Fig. 1** The mixture of deuterated and hydrogenous organic molecules self-assembles at the air-water interface as a monolayer and the gas species, NO₃ and NO₂, are expected to interact with both species. However, when monitoring the surface excess with neutron reflectometry, only the deuterated molecules are visible and hence the data collected provide information only on the reaction kinetic of the deuterated molecules. The red arrow shows chemical reaction, while the green arrows show the transport fluxes.
allowed us to follow the kinetics of the deuterated component and then reverse deuteration enabled us to follow the kinetics of the other surfactant with molecular resolution (see Fig. 1). The surface excess of the organic molecule during the oxidation reaction is monitored by NR at the air-ACMW (air-contrast matched water) interface, and information about reaction mechanisms can even be accessed thanks to partial deuteration of the surfactant. Furthermore, the surface composition of mixed systems can be resolved in situ during dynamic processes by the selective deuteration of different components, and therefore the reaction rates of individual components in mixtures can be determined. NR is an ideal technique to resolve kinetic and dynamic processes at fluid interfaces on the second time scale in the present work NR is used effectively to measure the surface excess of the deuterated component of binary surfactant mixtures during reactions with gas-phase NO2. NO3 is produced in situ by reacting O3 with NO2, the dependence of [NO3] on the initial [NO2] and [O3] is modelled, and to determine the concentration of NO3, the steady state concentrations of NO2 and N2O5 are measured using FTIR spectroscopy as a function of the initial [NO2].

The analysis of the kinetic experiments of the binary mixtures was based on the modelling approach developed in our previous work, where we took into account all the key reactions and processes. Briefly, in order to describe the NO3-initiated oxidation, we used a model, which considers, in addition to reactions, other mechanisms, such as accommodation, desorption, competition for adsorption sites and transport of the gas-phase species (see Sebastiani et al.). This model builds on the formalism and terminology of the “PRA framework” (introduced by Pöschl, Rudich and Ammann). It is a combination of K2-SURF, kinetic double-layer surface model and KM-SUB, kinetic multi-layer model of aerosol surface and bulk chemistry, but has been adapted to a planar geometry (see Sebastiani et al.). KM-SUB and K2-SURF have been applied to describe a range of experimental datasets and conditions. Both models describe the evolution of the kinetic parameters of an organic droplet exposed to oxidants. We have adapted the model to a monomolecular organic layer at the air-water interface for analysis and interpretation of the experimental data presented here. In the binary mixture, only the surface excess of the deuterated component is detected and hence the kinetic modelling describes the reaction of the deuterated surfactant. The kinetic parameters embed both the oxidant and the cosurfactant effect on the reaction with the deuterated component. The kinetic analysis of the measured surface excess decays for the four reaction systems provides information on the rate coefficients of the heterogeneous reaction as well as indirect information on the effect of the co-surfactant and the formation of surface-active products. The results obtained for the different molecules will be discussed in relation of their chemical structures. Furthermore, the comparison between NO3 and other oxidants species indicates to what extent night-time oxidation is important to atmospheric aerosol ageing. We also estimated oxidant uptake coefficients and compared those to literature data on similar organic molecules that have been studied in the condensed phase (i.e. droplets or thick films).

2 Methods
2.1 Experimental
2.1.1 Materials. The organic monolayers are comprised of binary mixtures in equal proportion (in terms of moles) of the following deuterated and standard fatty acids: deuterated oleic acid (d33OA, CD(CD2)7CD═CD(CD2)CO2D, Sigma-Aldrich, isotopic purity ≥98%, purity 99%), oleic acid (CH3(CH2)7CH═

Scheme 1 Chemical structure of the organic molecules studied.
NO₂ and N₂O₅ were carried out using IR absorption spectroscopy to establish the concentrations, [NO₂] and [N₂O₅], and their uncertainties. Modelling of the well-known reaction NO₂ + O₂ → N₂O₅ was carried out using IR absorption spectrometry, and these results are shown in the ESI Section 1. As in our previous work on the oxidation of deuterated monolayers by NO₂ in a custom-made reaction chamber, we carried out this work on the FIGARO instrument at the Institut Laue-Langevin. As in our previous work on monomolecular films, high flux settings were used to maximise the data acquisition rate involving an incident angle, \( \theta \), of 0.62°, a wavelength, \( \lambda \), range of 2–20 Å, and a constant resolution in momentum transfer, \( q \), of 11% over the probed \( q \)-range of 0.007 to 0.07 Å⁻¹, where \( q = 4\pi \sin \theta /\lambda \).

Only a brief description of the physical basis of NR with reference to its application is given here while more details may be found in ref. 52, 57, 66 and 67. NR is a technique that allows measuring the surface excess of oil-like films at the air–water interface. Neutron scattering is related to the coherent cross sections of the atoms with which the neutrons interact, and these values vary non-monotonically for different isotopes of the same atom and different atoms across the periodic table. In particular, swapping hydrogen for deuterium changes significantly the scattering, and as such mixing of hydrogenous and deuterated materials enables contrast matching.

We followed the change in reflectivity of a deuterated monolayer at the air–water interface using the time-of-flight mode measuring the entire \( q \)-range stated above with respect to the time of the oxidation reaction. For a deuterated surfactant monolayer at the air–ACMW interface the reflectivity, \( R \), can be expressed by:

\[
R = \left( \frac{16\pi^2}{q^2} \right) b^2 n^2 \sin^2 \left( \frac{qd}{2} \right)
\]

where \( b \) is the scattering length of the surfactant, in fm, \( n \) is the number density, in \( \text{Å}^{-2} \), \( d \) is the thickness of the layer in \( \text{Å} \), and \( bn = \rho \) is the scattering length density. The surface excess, \( \Gamma \), is given by:

\[
\Gamma = \frac{1}{A_{hg}} = \frac{\rho d}{b}
\]

where \( A_{hg} \) is the area per molecule (or per head group). The surface excess, \( \Gamma \), is calculated from the scattering length density, \( \rho \), which results from fitting the reflectivity profile with the eqn (1) as a model. A surface excess for insoluble molecules corresponds to surface concentration.

A stratified layer model was applied to the experimental data involving a single layer for the deuterated surfactant. It has been shown that in this low \( q \)-range (<0.07 Å⁻¹), the value of \( \Gamma \) is very insensitive to specific details of the model applied. Fitting of the thickness with an arbitrary fixed value of the density or fitting of the density with an arbitrary fixed value of the thickness (to within reasonable bounds) gives equivalent results to within an added uncertainty of less than 2%. In our case, we chose to fit \( \rho \) while fixing \( d \) at the value obtained by fitting data recorded over a wider \( q \)-range (up to 0.25 Å⁻¹).

Normalisation of the reflectivity data was carried out with respect to the total reflection of an air–D₂O measurement. The sample stage was equipped both with passive and active anti-vibration controls. The reaction chamber was mounted on the sample stage, interfaced with the gas setup, and the trough (13 × 10 cm) was filled with 80 ml of ACMW. A fixed amount of solution was spread using a microlitre Hamilton syringe in order to form the monolayer following the protocol used in other NR studies of atmospheric relevance. The volume of solution spread was 26 µl for \( d_{33}\text{-OA-hMO} \), 25 µl for \( d_{33}\text{-OA-hSA} \), 27 µl for \( d_{33}\text{-MO-hOA} \) and 29 µl for \( d_{33}\text{-MO-hSA} \). The solvent was allowed to evaporate before closing the chamber. Since we used a barrier-less trough the desired surface pressure (16 to 25 mN m⁻¹ depending on the molecule) was achieved by spreading a calculated number of molecules on the surface as described earlier.

From the surface excess obtained by NR the reproducibility is found to be within 1 to 14%, depending on the binary mixture. The choice of initial surface pressure and surface excess was based on the requirement of maximising the signal-to-noise ratio for NR measurements while having a reaction that lasts long enough to be analysed for kinetic parameters. A reduction of the initial surface pressure is not expected to affect the kinetic behaviour, i.e. the \( \Gamma(t) \) will start from a lower value and the curve will extend on a shorter time and less data will be available for the kinetic fitting. The monolayer was further characterised with compression-expansion isotherms with a Langmuir trough off-line, while recording Brewster-angle microscopy (BAM) images at different surface pressure values, and these results are shown in the ESI Section 1. Data were recorded for several minutes before NO₂ was admitted into the reaction chamber. The time resolution was set to 2 s. The alignment of the interface was maintained to a precision of

<table>
<thead>
<tr>
<th>NO₂/molecule per cm³</th>
<th>NO₂/ppt</th>
<th>NO₂ flow rate/dm³ min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3.5 ± 1.5) × 10⁸</td>
<td>13 ± 5</td>
<td>0.360</td>
</tr>
<tr>
<td>(4.2 ± 1.4) × 10⁸</td>
<td>15 ± 5</td>
<td>0.290</td>
</tr>
<tr>
<td>(6.1 ± 1.2) × 10⁸</td>
<td>23 ± 4</td>
<td>0.200</td>
</tr>
<tr>
<td>(9 ± 3) × 10⁸</td>
<td>32 ± 10</td>
<td>0.160</td>
</tr>
<tr>
<td>(10 ± 3) × 10⁹</td>
<td>36 ± 10</td>
<td>0.130</td>
</tr>
<tr>
<td>(9.3 ± 2.4) × 10⁸</td>
<td>35 ± 9</td>
<td>0.104</td>
</tr>
<tr>
<td>(2.3 ± 1.2) × 10⁹</td>
<td>86 ± 45</td>
<td>0.08</td>
</tr>
<tr>
<td>(2.6 ± 1.0) × 10⁹</td>
<td>100 ± 40</td>
<td>0.06</td>
</tr>
</tbody>
</table>
and the bulk (b), following the formalism of Shiraiwa et al.60 (as illustrated in Fig. 1).

Gas-phase species (NO₃ and NO₂) can adsorb to the sorption layer and interact with the organic molecules in the surface layer. The reaction products can stay at the surface layer, or they can be lost through solubilisation into the bulk or by evaporation into the gas phase.

The evolution of the gas species surface concentration, [X]ₜₕ, is described by considering adsorption, desorption, transport and reaction (see ESI† for further details). The key equations that describe the reactions are discussed below (the nomenclature is based on the PRA framework58–60,69,78).

In the model, the gas-phase compound NO₃ reacts with the organic layer and its loss, Lₜₕ,Y,NO₃, is described with the second-order rate coefficient kₜₕ,Y,NO₃:

\[ L_{t,NO_3} = k_{t,NO_3}[Y]_{ss}[NO_3]_b \]  

(3)

The evolution of the NO₃ surface and bulk concentrations can be described as:

\[ \frac{d[NO_3]_b}{dt} = J_{ads,NO_3} - J_{des,NO_3} - L_{surf,Y,NO_3} + J_{sb,NO_3} - J_{sb,NO_3} \]  

(4)

\[ \frac{d[NO_3]_b}{dt} = \left( J_{sb,NO_3} - J_{sb,NO_3} \right) \frac{A}{V} \]  

(5)

where A is the water surface area and V is the total water volume. The flux of adsorbed gas molecules, \( J_{ads,NO_3} \), is proportional to the surface accommodation coefficient, \( \alpha_{s,NO_3} \), which is determined by the product of the surface accommodation coefficient on an adsorbate-free surface, \( \alpha_{s,NO_3} \), and the sorption layer coverage, \( \theta_s \), given by the sum of the surface coverage of all competing adsorbate species. The flux of desorption, \( J_{des,NO_3} \), is proportional to the inverse of the desorption lifetime, \( \tau_{d,NO_3} \), which is the average time that the NO₃ molecule occupies an adsorption site. \( \tau_{d,NO_3} \) is a combination of two desorption lifetimes, depending on the adsorption state of the NO₃ molecule, at the interface, \( \theta_{ss} = [Y]_{ss}(0)/[Y]_{ss}(0) \); either closely packed \( (\tau_{d,NO_3}^{-1}) \), or in the gas-like state \( (\tau_{d,NO_3}^{-1}) \):

\[ J_{des,NO_3} = k_{d,NO_3}[NO_3]_b \tau_{d,NO_3}^{-1} \]  

(6)

\[ \tau_{d,NO_3}^{-1} = \theta_{ss} \tau_{d,NO_3,ss}^{-1} + (1 - \theta_s) \tau_{d,NO_3,gb}^{-1} \]  

(7)

The organic reactant, Y (e.g. oleic acid) is lost only through reaction with NO₃ at the surface, described as:

\[ \frac{d[Y]_s}{dt} = -k_{surf,Y,NO_3}[Y]_{ss}[NO_3]_b \]  

(8)

The products (Z) of the heterogeneous reaction cannot be identified individually at the air–water interface in our experiments, so we described them as three key categories: surface-active (i.e. remaining at the surface and directly measurable by NR, Zₕ), volatile (i.e. escaping into the gas-phase, Zₕ) and soluble (i.e. accumulating in the water bulk, Zₕ) compounds. Since the surface-active products (Zₕ) will remain at the air–water interface, the surface–bulk transport is negligible:
\[
\frac{d[Z_{\text{s,\text{sur}}}]}{dt} = c_{k_{\text{surf,\text{NO}_3}}} [X]_{\text{sur}} [\text{NO}_3]_s
\]

where \(c_k\) is the branching ratio for the surface-active products. The volatile products \((Z_v)\) will leave the surface based on their vapour pressures. The soluble products \((Z_s)\) will diffuse into the water bulk depending on the diffusion coefficient. All equations describing the evolution of the various species can be found in the ESI. This system of equations cannot be solved analytically, hence the ODE solver of MATLAB® (2011) has been used for numerical solving. In order to fit \(I(t)\), provided by NR, a minimisation of the value of \(\chi^2\) has been performed using the FMINUIT package.79

3 Results and discussion

Two of the organic molecules considered in this work (OA and MO) contain one unsaturated C–C bond in the aliphatic tail while one molecule (SA) is fully saturated. Among the unsaturated surfactants, MO is a methyl ester in comparison with the fatty acid OA. The double bond is expected to be the key reactive site for NO3. Kinetic data on the two reactive unsaturated surfactants in the presence of a co-surfactant are presented in Sections 3.1 and 3.2. When a deuterated surfactant is mixed with a hydrogensous surfactant the reaction of the first molecule can be followed in the presence of the second. Each section will illustrate the data collected for the 1 : 1 mixture (by mole) of deuterated and hydrogensous same molecule, then the deuterated surfactant mixed with saturated molecule (SA) and finally the deuterated surfactant mixed with the other unsaturated molecule in its hydrogensous form.

3.1 Oleic acid (\(d_{34}\)OA) exposed to nitrate radicals (NO3) in the presence of a co-surfactant

We investigated the time evolution of the two-component films when following the decay of deuterated oleic acid (\(d_{34}\)OA) component mixed with hydrogensous oleic acid (dOAhOA), the saturated surfactant stearic acid (dOAhSA) and its methyl ester (dOAhMO). Fig. 2 shows the surface excess decays of \(d_{34}\)OA monolayers at the air–ACMW interface as a function of time with respect to different \([\text{NO}_3]\) in the presence of hOA, hSA and hMO. The NO\textsubscript{2}-initiated oxidation leads to a non-zero surface excess value (4–6 × 10\textsuperscript{13} molecule per cm\textsuperscript{2}) at the end of the reactive decay. This plateau value is reached following an initial decay, which lasts between 5 min and well over 1 h depending on \([\text{NO}_3]\). \([\text{NO}_3]\) ranges from (13 ± 6) to (86 ± 45) ppt. For several gas conditions, the oxidation was carried out twice, demonstrating a good reproducibility for high \([\text{NO}_3]\) (~35 ppt), and visually higher variability for lower concentrations. However, the uncertainty in \([\text{NO}_3]\), for \([\text{NO}_3] < 35\) ppt, is ~30%, which means that even a small variation in concentration produces a measurable change in the rate of loss of the deuterated surfactant. The oxidant is admitted into the chamber at \(t = 0\) s, and the decay of the surface excess starts almost immediately suggesting that the monolayer begins to be consumed as soon as the oxidant is admitted. The surface excess of \(d_{34}\)OA was monitored also for exposure to O\textsubscript{2} when mixed with hSA and hMO, and for exposure to NO\textsubscript{2} only when mixed with hMO in order to assess a mechanical loss due to gas flux and isomerisation effects due to the presence of O\textsubscript{2} (compare to King et al.\textsuperscript{79}). All blanks show a very stable surface excess for \(d_{34}\)OA over the relevant timescale. The O\textsubscript{2} blank for \(d_{34}\)OA-hMO shows a surface excess fluctuation of about 5%; this may be due to some mechanical vibrations or other intermittent interference during this particular experimental run, but given the stability of this film in the presence of NO\textsubscript{2} (and all other films in the presence of O\textsubscript{2}) and the fact that the reactive decays are all very clearly distinct from the apparent, but comparatively small fluctuations in this run, we did not explore these fluctuations further within the tight timeframe of these neutron beamtime experiments.

The kinetic fitting was performed taking into account the variability of the gas concentrations (both for NO\textsubscript{2} and NO\textsubscript{3}) and the initial surface excess was set to a value that takes into account only the \(d_{34}\)OA, since the hydrogenous surfactant was effectively invisible to the NR technique (the scattering length of the hydrogenous material is only about 1% of the deuterated form). An example of the kinetic fit is displayed in Fig. 2C (see Section 3.2 of the ESI† for the complete data set). The modelling of the data followed the same approach as that for the single component monolayers;\textsuperscript{79,*} the kinetic parameters are discussed in comparison to the results for single molecule monolayers.

Fig. 2 Surface excess decays of dOAhOA (A), dOAhSA (B) and dOAhMO (C) exposed to different [NO\textsubscript{3}]; mean values of NO\textsubscript{3} mixing ratios are displayed in the legend (1 ppt = 2.7 × 10\textsuperscript{7} molecule per cm\textsuperscript{3}). NO\textsubscript{3} is admitted at \(t = 0\) s. In the insert, data and fit are shown for dOAhMO exposed to [NO\textsubscript{3}] = 86 ppt.
reported earlier with our new data allowing us now to explore the effect of the co-surfactant presence which is crucial to link the results for the frequently studied monomolecular films to complex, multi-component surfactant materials encountered in the real atmosphere.

The range of data we used for the kinetic fitting starts very close to the beginning of the reactive decay when NO3 is admitted to the chamber \(t = 0\) s, and ends at a surface excess of \(5 \times 10^{-13}\) molecule per cm\(^2\): data below this value are excluded from the fitting for two main reasons: (i) at low coverage the data become more sensitive to experimental details such as the precise background subtraction, so the parameters that affect the kinetic model are better determined without increasing sensitivity to these factors; and (ii) at low coverage some surfactants can segregate into domains which are inhomogeneous laterally (especially when mixing saturated and unsaturated surfactants), and the NR model does not have the resolution to distinguish this effect but the results are modestly affected, so again it is better to desensitize the kinetic parameters from this effect. The fitted curve, which results from the sum of the surface excesses of \(d_{34}\)OA and the products, is shown as a solid red line in the insert of Fig. 2C. Since NR effectively measures the quantity of deuterium atoms at the air–ACMW interface, a distinction between reactant and products is not possible from NR data; hence the fitting function needs to take into account the contribution to \(I\) from both \(d_{34}\)OA and its reaction products. The product yields are taken from our previous work; we assumed that at \(t = 0\) s the signal is arising solely from \(d_{34}\)OA, while the signal for long reaction time when the reactive decay has ceased (e.g. \(t > 1000\) s for [NO\(_3\)] = 86 ppt) is entirely due to the surface-active products. Also, the products are assumed to have a similar scattering length density to \(d_{34}\)OA, since oxidation of \(d_{34}\)OA is expected to break the molecule into two parts, which each maintains almost the same ratio between scattering length and molecular volume. The scattering length of the products is thus likely to be \(ca.\) half of the scattering length of \(d_{34}\)OA and the product film also likely possesses \(ca.\) half of the \(d_{34}\)OA film thickness. Given this, and considering eqn (2), the resulting surface excess of the products corresponds to the value calculated with \(\rho, d\) and \(b\) of \(d_{34}\)OA. This approximation is not valid in the extreme case of the products being only surface-active, since the packing would be two times denser that for oleic acid, and this should be considered in the surface excess calculation and consequent modelling. In our study, the surface-active product yield is between 22% and 33%, and it has been taken into account that the total number of product molecules (surface-active, volatile and soluble) was twice the number of the reactant molecules.

Following the approach we used for the single component monolayer, the accommodation coefficients for the gas-phase species were fixed to one, and the desorption lifetimes were left free to vary in the range \(10^{-9}\) to \(10^{-7}\) s, which is in agreement with the values suggested by Shiraiwa et al. For the rate coefficient, the range of variability was optimised through a sensitivity study performed by changing in the Matlab code the value of \(k_{surf}\). The suitable range of values found was \((0.7–8) \times 10^{-7}\) cm\(^2\) per molecule per s, which is significantly higher than the best fit value provided by Shiraiwa et al. for abietic acid exposed to NO\(_3\) (1.5 \(\times 10^{-9}\) cm\(^2\) per molecule per s) and wider than the range used for the single component monolayer study. The optimisation of the kinetic parameters was performed systematically by the \(\chi^2\) minimisation routine FMINUIT. The sensitivity of the model to changes in desorption lifetimes is shown in the ESL.

Fig. 3 The evolution of the surface concentrations obtained from kinetic modelling using the best-fitted parameters for the data shown in Fig. 2C and 4C for (A) the organic reactant \(Y\) respectively doOA mixed with hMO (blue) and dMO mixed with hOA (black) exposed to [NO\(_3\)] = 86 ppt; (B) the surface concentration for the gas-phase species NO\(_3\) reacting with dOAhMO (blue) and dMOhOA (black); and the surface-active \((Z_s)\), volatile \((Z_v)\) and soluble \((Z_s)\) products produced by dOAhMO (C) and dMOhOA (D).
Table 2. Results of the kinetic modeling of the experimental data for the d_{34}OA-hOA, d_{34}OA-hSA, d_{34}MO-hMO, d_{34}MO-hSA and d_{34}MO-HOA systems. The results for the monomolecular layer are reported for comparison. The uncertainties correspond to one standard deviation.

<table>
<thead>
<tr>
<th>Modelling parameter</th>
<th>Best fit values</th>
<th>Values from Sebastiani et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{\text{obs}, \text{OA-hOA}} ) (cm² per molecule per s)</td>
<td>2.8 ± 0.7 (0.7–4)</td>
<td>3.2 ± 0.2 (0.7–8)</td>
</tr>
<tr>
<td>( k_{\text{obs}, \text{OA-hSA}} ) (cm² per molecule per s)</td>
<td>2.8 ± 0.7 (0.7–4)</td>
<td>3.2 ± 0.2 (0.7–8)</td>
</tr>
<tr>
<td>( k_{\text{obs}, \text{MO-hMO}} ) (cm² per molecule per s)</td>
<td>3.3 ± 1.0 (0.7–6)</td>
<td>3.0 ± 0.6 (0.7–8)</td>
</tr>
<tr>
<td>( k_{\text{obs}, \text{MO-hSA}} ) (cm² per molecule per s)</td>
<td>3.3 ± 1.0 (0.7–6)</td>
<td>3.0 ± 0.6 (0.7–8)</td>
</tr>
<tr>
<td>( k_{\text{obs}, \text{OA-HOA}} ) (cm² per molecule per s)</td>
<td>3.3 ± 1.0 (0.7–6)</td>
<td>3.0 ± 0.6 (0.7–8)</td>
</tr>
<tr>
<td>( k_{\text{obs}, \text{MO-HOA}} ) (cm² per molecule per s)</td>
<td>3.3 ± 1.0 (0.7–6)</td>
<td>3.0 ± 0.6 (0.7–8)</td>
</tr>
</tbody>
</table>

Modelled evolutions of the concentrations of reactants and products are exemplified in Fig. 3 with examples taken for the mixtures dOAhMO and dMOhOA. Fig. 3A shows the model for the surface excess of dOA in the mixture dOAhMO and of dMO in the mixture dMOhOA. The steady state [NO₃]ₕ for the two mixtures reaches different values (see Fig. 3B): [NO₃]ₕ reaches a ca. 40% higher value when reacting with dOAhMO than with dMOhOA. This has two reasons: (i) the difference in the initial NO₃ gas-phase concentration, in fact while both experimental runs had the same settings for the NO₃ production, the uncertainty in the NO₃ concentration is about 50% (see Table 1) and hence the model accounts for this variability with the best fit for the initial NO₃ gas concentration being 27% higher for dOAhMO than for dMOhOA; (ii) the desorption lifetime at low coverage, \( t_{\text{d,NO₃}} \), determines how long the NO₃ remains at the sorption layer, and this lifetime is about 60% longer for dOAhMO compared to dMOhOA. Fig. 3C and D show the time evolution of the products; the difference in the amounts of surface-active products, \( Z_a \) and soluble products, \( Z_b \), depends on the product yields for OA and MO, while the total amount of volatile product, \( Z_G \), is comparable for the two reactants if normalized by the respective starting [Y]₀.

While visually the \( Z_G \) peak is significantly higher for dOAhMO compared to dMOhOA, when comparing the areas below the curves (noting the different timescales for the two reactions), the total amount of \( Z_G \) for dOAhMO is about 33% higher than for dMOhOA, which is due to the initial reactant amounts differing by about 20% and the fact that reaction for dOAhMO is complete while it is not for dMOhOA (see differences in the surface excesses at \( t = 0 \) and at the last time point in Fig. 3A).

This fitting approach has been applied to all the molecules studied, while accounting for different product yields and kinetic parameter ranges (see Table 2).

The kinetic parameters related to the products, which have been used as fixed input parameters, are taken from our previous work with single component monolayers. The product yields were optimised to \( c_\text{OA} = 0.2 \) for the surface-active products, \( c_\text{OA} = 0.45 \) for the volatile products and \( c_\text{OH} = 0.35 \) for the soluble products. The best fit values for the kinetic parameters related to the heterogeneous reaction between \( \text{d}_{34}\text{OA} \) and NO₃ in the presence of hOA, hSA and hMO are summarised in Table 2. The presence of a co-surfactant can have different effects on the kinetics of the reaction occurring between \( \text{d}_{34}\text{OA} \) and NO₃: for example, the co-surfactant can have a higher reaction rate and compete for NO₃ uptake. Within the monolayer, the co-surfactant will occupy a different area per molecule than \( \text{d}_{34}\text{OA} \); the area will be larger for hMO and smaller for hSA, thus affecting the packing and the availability of the C=C double bond of \( \text{d}_{34}\text{OA} \) for NO₃ adsorption. We measured the reaction of \( \text{d}_{34}\text{OA} \) in the presence of hOA in order to determine the effect of monitoring the surface excess of only half the molecules exposed to NO₃ and we found similar results as for the fully deuterated monolayer. The rate coefficient for \( \text{d}_{34}\text{OA-hOA} \) exposed to NO₃ was found to be \( (3.2 ± 0.2) \times 10^{-5} \) cm² per molecule per s. The fast desorption time obtained for NO₃ is \( (8 ± 2) \times 10^{-9} \) s and the slow desorption is about 2.5 times longer, while the desorption time for NO₂ (NO₂ is present in our NO₃ oxidation experiments together with O₃) is four times
longer. The introduction of two desorption times reflects the change of orientation of the organic molecules at the interface, i.e. for a highly packed monolayer the reactive site is less accessible, and the oxidant has less affinity for other parts of the molecules hence the desorption is faster. When the organic surface coverage decreases the reactive sites become more accessible and the desorption is slowed down.

The rate coefficient for \( d_{33}\text{OA-hSA} \) exposed to \( \text{NO}_3 \) was found to be \( (3.6 \pm 0.9) \times 10^{-8} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1} \). It should be noted that the loss of surfactant material due to \( \text{O}_2 \) flow only (see black symbols in Fig. 2) leads to an apparent loss rate coefficient in the order of \( 10^{-11} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1} \), which is well within the uncertainty of the reactive rate coefficient. The fast desorption time obtained for \( \text{NO}_3 \) is \( (14 \pm 4) \times 10^{-9} \text{ s} \) and the slow desorption is about the same value, while the \( \text{NO}_2 \) desorption time is about three times longer. The fast desorption time obtained for \( \text{NO}_3 \) is about three times longer, while the \( \text{NO}_2 \) desorption time is about three times longer. The fact that \( \tau_{d,\text{NO}_3,1} \) and \( \tau_{d,\text{NO}_3,2} \) have similar values agrees well with the idea that the area per molecule of \( d_{33}\text{OA} \) is larger and the \( \text{C} = \text{C} \) double bond is more readily available when mixed with the same number of hSA molecules than when in a pure system, hence hSA has a smaller area per molecule and packs more tightly than OA (see section 1 of ESI†).

The rate coefficient for \( d_{33}\text{OA-hMO} \) exposed to \( \text{NO}_3 \) was determined to be \( (3 \pm 3) \times 10^{-9} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1} \). The loss due to \( \text{O}_2 \) flow alone leads to an apparent rate coefficient in the order of \( 10^{-11} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1} \), which is again well within the uncertainty of the reactive rate coefficient. The fast desorption time obtained for \( \text{NO}_3 \) is \( (8 \pm 3) \times 10^{-9} \text{ s} \) and the slow desorption is about three times longer, while the \( \text{NO}_2 \) desorption time is about five times longer. These values are comparable with those found for \( d_{33}\text{OA-hOA} \) which suggests that hMO has no major effect on OA oxidation kinetics, while the presence of SA slightly increases the rate coefficient and prolongs the fast desorption time both leading to a faster surface excess decay.

### 3.2 Methyl oleate (\( d_{33}\text{MO} \)) exposed to nitrate radicals (\( \text{NO}_3 \)) in the presence of a co-surfactant

Methyl oleate (MO) differs from OA in terms of the head group: instead of a carboxylic acid it has a methyl ester (\( \text{COOCH}_3 \)) group. \( d_{33}\text{MO} \) was used to study the oxidation by \( \text{NO}_3 \) in the presence of a hydrogensurfactant: hMO, hSA and hOA (see Table 1 in the ESI†). MO occupies a larger surface area and is less stable at the air–water interface than OA because of its less hydrophilic head group. However, the reactive site is in a very similar chemical environment as for OA, and any difference in reaction kinetics is expected to be related to the chain orientation and formation of different products.

![Image](https://example.com/image1.png)

**Fig. 4** Surface excess decays of \( \text{dMOhMO} \) (A), \( \text{dMOhSA} \) (B), and \( \text{dMOhOA} \) (C) exposed to different \( [\text{NO}_3] \); mean values of \( \text{NO}_2 \) mixing ratios are displayed in the legend (1 ppt = \( 2.7 \times 10^7 \) molecule per \( \text{cm}^3 \)). \( \text{NO}_3 \) is admitted at \( t = 0 \) s. In the insert, data and fit are shown for \( \text{dMOhSA} \) exposed to \( [\text{NO}_3] = 86 \) ppt.
The fast desorption time obtained for NO$_3$ is (8 ± 2) × 10$^{-9}$ s and the slow desorption is about four times longer, while the NO$_2$ desorption time is six times longer. The rate coefficient for $d_{33}$MO-hSA exposed to NO$_3$ was found to be (3 ± 1) × 10$^{-8}$ cm$^2$ per molecule per s. The fast desorption time obtained for NO$_3$ is (21 ± 10) × 10$^{-9}$ s and the slow desorption is about the same value, while the NO$_2$ desorption time is about 50% longer. As for $d_{33}$OA, $\tau_{d,NO_3}$ and $\tau_{d,NO_2}$ have similar values and this agrees well with the idea that the area per molecule of $d_{33}$MO is larger and C=O double bond is more readily available when mixed with the same number of hSA molecules than when in a pure system, since hSA has a smaller area per molecule and packs tighter than MO (see section 1 of the ESI†).

The rate coefficient for $d_{33}$MO-hOA exposed to NO$_3$ was found to be (0.7 ± 0.4) × 10$^{-8}$ cm$^2$ per molecule per s. The fast desorption time due to O$_2$ flow only leads to an apparent rate coefficient on the order of 10$^{-10}$ cm$^2$ per molecule per s, which is well within the uncertainty of the reactive rate coefficient. The fast desorption time obtained for NO$_3$ is (12 ± 3) × 10$^{-9}$ s and the slow desorption is about 50% longer, while the NO$_2$ desorption time is about three times longer. Interestingly, this rate coefficient is significantly smaller than those found for $d_{33}$MO-hMO and $d_{33}$MO-hSA, while the desorption times are comparable for all these systems. We were thus able to quantitatively demonstrate that hOA has a significant influence on DMO oxidation kinetics. The importance in the atmospheric context of this experimental finding of a substantially altered reactive decay due to the presence of a co-surfactant will be discussed in the subsequent section on Atmospheric implications. hOA leaves surface active products upon NO$_3$-initiated oxidation, and those products may compete with MO for the NO$_3$ uptake or they can arrange around MO molecules making the double bonds less accessible and hence slow down the reaction. All fits are presented in the ESI.†

### 4 Atmospheric implications

The kinetic parameters obtained by analysing the NR data allowed investigation of the effects of co-surfactants in binary mixtures. This is a key step from the monomolecular films that are commonly studied in the laboratory environment towards an understanding of how these laboratory-based kinetic results can be linked to processes happening in the atmosphere where surfactants will exist in a complex matrix of other species including a wide range of saturated and unsaturated surfactants that are most likely to affect the structure at the air–water interface and thus potentially impact on the reactive decay of unsaturated surfactants such as oleic acid. We have carefully selected closely related surfactants that represent saturated (stearic acid) and unsaturated (oleic acid/methyl oleate) species found in the atmosphere. Thanks to our previous work in the same experimental set-up on these species as monomolecular films, we could focus this study on the quantitative differences in the presence of co-surfactant by selective deuteration of first one and then the other of the species in the binary mixtures.

As outlined above, most mixtures tested do not show substantially different kinetic behaviours ($k_{surf}$ is in the range of 2.8 to 4.1 × 10$^{-8}$ cm$^2$ per molecule per s) and the small differences in $k_{surf}$ and the desorption times can be explained by the different structures at the air–water interface that will affect the accessibility of the C=C double bond for the NO$_3$ radicals.

The most striking result was found when following the decay of dMO in a binary mixture with hOA. We determined a ca. six times slower decay for dMO-hOA compared to dMO-hMO ((0.7 ± 0.4) × 10$^{-8}$ cm$^2$ per molecule per s compared to (4.1 ± 0.8) × 10$^{-8}$ cm$^2$ per molecule per s). We calculated the uptake coefficients for all the binary mixtures (see Table 3) to allow comparison with data collected in different experimental setups, where the direct result is the NO$_3$ uptake coefficient; and again, we found a lower uptake of NO$_3$ by dMO-hOA compared to the other mixtures. This difference lies well outside the experimental uncertainty and demonstrates that matrix effects of co-surfactants can indeed affect the reaction kinetics and data from monomolecular surfactant experiments cannot simply be added up to understand the decay of these species in more complex and atmospherically relevant mixtures. Such a retardation of oxidative decay was not found for the binary mixtures of the surfactants OA and SA with a carboxylic acid headgroup. It thus seems likely that the less stable species at the air–water interface (such as MO with its methyl ester headgroup and more limited lifetime at the interface) may be more strongly affected

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$k_{surf}$/cm$^2$ per molecule per s</th>
<th>$\gamma$/10$^3$</th>
<th>$\gamma_{	ext{lit}}$/10$^3$</th>
<th>Lifetime$^b$/minute</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{33}$OA</td>
<td>(2.8 ± 0.7) × 10$^{-8}$c</td>
<td>2.1 ± 0.5$^c$ (3 ± 1) × 10$^{-9}$d [1.6 ± 0.3]$^c$</td>
<td>6.0 ± 1.5$^c$</td>
<td>5.0 ± 0.3</td>
</tr>
<tr>
<td>$d_{33}$OA-hOA</td>
<td>(3.2 ± 0.2) × 10$^{-8}$c</td>
<td>2.6 ± 0.2</td>
<td>5 ± 1</td>
<td></td>
</tr>
<tr>
<td>$d_{33}$OA-hSA</td>
<td>(3.6 ± 0.9) × 10$^{-8}$c</td>
<td>3.4 ± 0.8</td>
<td>6 ± 2</td>
<td></td>
</tr>
<tr>
<td>$d_{33}$OA-hMO</td>
<td>(3 ± 1) × 10$^{-8}$c</td>
<td>2.6 ± 0.8</td>
<td>5 ± 1</td>
<td></td>
</tr>
<tr>
<td>$d_{33}$MO</td>
<td>(3.3 ± 0.6) × 10$^{-8}$c</td>
<td>2.1 ± 0.4$^c$ [1.4$^{+0.8}_{-0.5}$] × 10$^{-9}$d</td>
<td>4.0 ± 0.8</td>
<td>5 ± 2</td>
</tr>
<tr>
<td>$d_{33}$MO-hMO</td>
<td>(4.1 ± 0.8) × 10$^{-8}$c</td>
<td>2.8 ± 0.5</td>
<td>22 ± 13</td>
<td></td>
</tr>
<tr>
<td>$d_{33}$MO-hSA</td>
<td>(3 ± 1) × 10$^{-8}$c</td>
<td>2.2 ± 0.7</td>
<td>5 ± 2</td>
<td></td>
</tr>
<tr>
<td>$d_{33}$MO-hOA</td>
<td>(0.7 ± 0.4) × 10$^{-8}$c</td>
<td>0.5 ± 0.3</td>
<td>22 ± 13</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Calculated as $k_{surf} \times A = [Y]_0$ with $A$ a gas constant in seconds and $[Y]_0$ the surface concentration of the deuterated molecule, see ref. $^{41}$. $^b$ See ref. $^{11}$ for details on the lifetime calculation. $^c$ Values determined in our previous work. $^d$ Value refers to a study with a flow tube coupled to a chemical ionisation mass spectrometer. $^e$ Value refers to 1-octadecene uptake measured in a rotating wall flow tube. $^f$ Value refers to binary mixtures of MO and saturated molecules measured in a rotating wall flow tube.
by co-surfactant effects. These species are harder to study experimentally because of exactly this less stable nature. While there is a considerable uncertainty about the relative proportions of the head groups in surface-active material in the atmosphere, it is clear that fatty acids as well as esters are key classes (e.g. Cheng et al.85). For instance, sea spray aerosols collected over the Mediterranean Sea contained C14 to C34 fatty acid methyl esters (mainly methyl palmitate and methyl stearate).84,85 Degradation of particulate matter suspended in seawater by marine organisms has been shown to be a key source of saturated and unsaturated fatty acid methyl esters.86 Overall, it seems very likely that atmospheric surface-active materials will not be limited to perfectly hydrophilic headgroups that are most frequently studied in the laboratory. This new insight into the ageing of multi-component monolayers is thus of particular relevance for the formation of secondary organic aerosols in the atmosphere as well as clouds.

5 Conclusion

In summary, our results provide clear evidence that multi-component mixtures need to be carefully considered when trying to establish the lifetimes of films in the atmosphere. Simply adding up kinetic data obtained for monomolecular films in the laboratory are unlikely to yield realistic residence times especially if non-perfect headgroups are present in the surface-active material of interest. We could quantify the retardation of the kinetic decay by NO3 to be ca. a factor of six for the dMO/hOA binary mixture. This would cause the residence time to change from ca. 4 to 22 minutes and could thus lead to substantially increased transport distances of surfactant species together with any other pollutants that may be protected underneath the surfactant film.

Data availability


Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

The authors would like to thank Dr Francesco Piscitelli, Dr Ernesto Scoppola and Dr Kunal Rastogi for the help during the night shifts on FIGARO. We would like to thank the Partnership for Soft Condensed Matter for access to the ellipsometer, and the ILL (Grenoble, France) for allocations of beam time on FIGARO. We are grateful for technical support at ILL from Simon Wood. FS is grateful for support from the ILL and the University of Reading in the framework of the NEATNOX studentship. CP thanks NERC (grant number NE/G000883/1) for support.

References

14 V. Gérard, B. Noziere, L. Fine, C. Ferronato, D. K. Singh,
A. A. Frossard, R. C. Cohen, E. Asmi, H. Lihavainen,
N. Kivekäs, M. Aurela, D. Brus, S. Frka and A. Cvitešić Kušan, Concentrations and Adsorption Isotherms for
12388.
15 B. Woden, M. W. A. Skoda, A. Milsom, C. Gubb, A. Maestro,
J. Tellam and C. Pfang, Ozonolysis of fatty acid monolayers
at the air-water interface: organic films may persist at the
surface of atmospheric aerosols, Atmos. Chem. Phys., 2021,
21, 1325–1340.
16 E. Adams and H. Allen, Palmitic Acid on Salt Subphases and
in Mixed Monolayers of Cerebrosides: Application to
Atmospheric Aerosol Chemistry, Atmosphere, 2013, 4, 315–
336.
17 H. Tervahattu, J. Juhanoka and K. Kupiainen, Identification
of an organic coating on marine aerosol particles by TOF-
18 H. Tervahattu, K. Hartonen, V.-M. Kerminen, K. Kupiainen,
P. Aarnio, T. Koskentalo, A. F. Tuck and V. Vaidaa, New
evidence of an organic layer on marine aerosols, J.
19 P. Q. Fu, K. Kawamura, J. Chen, B. Charrière and R. Sempéré,
Organic molecular composition of marine aerosols over
the Arctic Ocean in summer: contributions of primary emission
and secondary aerosol formation, Biogeosciences, 2013, 10,
653–667.
20 J. D. Allan, P. I. Williams, W. T. Morgan, C. L. Martin,
21 Q. Wang, X. He, M. Zhou, D. D. Huang, L. Qiao, S. Zhu,
Y. Ma, H. Wang, L. Li, C. Huang, X. H. H. Huang, W. Xu,
23 R. Ots, M. Vieno, J. D. Allan, S. Reis, E. Nemitz, D. E. Young,
H. Coe, C. Di Marco, A. Detournay, I. A. Mackenzie,
24 A. L. Robinson, N. M. Donahue and W. F. Rogge,
Photochemical oxidation and changes in molecular composition of organic aerosol in the regional context, J.
25 M. Kang, F. Yang, H. Ren, W. Zhao, Y. Zhao, L. Li, Y. Yan,
Y. Zhang, S. Lai, Y. Zhang, Y. Yang, Z. Wang, Y. Sun and
P. Fu, Influence of continental organic aerosols to the
marine atmosphere over the East China Sea: Insights from
26 A. Milsom, A. M. Squires, J. A. Boswell, N. J. Terrill,
A. D. Ward and C. Pfang, An organic crystalline state in
ageing atmospheric aerosol proxies: spatially resolved structural changes in levitated fatty acid particles, Atmos.
27 Q. Mu, M. Shiraiwa, M. Octaviani, N. Ma, A. Ding, H. Su,
G. Lammel, U. Pöschl and Y. Cheng, Temperature effect on
phase state and reactivity controls atmospheric multiphase
chemistry and transport of PAHs, Sci. Adv., 2022, 4, eaap7314.
28 M. Shrivastava, S. Lou, A. Zelenyuk, R. C. Easter, R. A. Corley,
B. D. Thrall, P. J. Rasch, J. D. Fast, S. L. Massey Simonich,
H. Shen and S. Tao, Global long-range transport and lung
29 R. P. Wayne, I. Barnes, P. Biggs, J. P. Burrows, C. E. Canosa-
Mas, J. Hjorth, G. Le Bras, G. K. Moortgat, D. Perner,
G. Poulet, G. Restelli and H. Sidebottom, The nitrate
radical: physics, chemistry, and the atmosphere, Atmos.
30 N. Mora-Diez and R. J. Boyd, A Computational Study of the
Kinetics of the NO3 Hydrogen-Abstraction Reaction from
31 N. L. Ng, S. S. Brown, A. T. Archibald, E. Atlas, R. C. Cohen,
J. N. Crowley, D. A. Day, N. M. Donahue, J. L. Fry, H. Fuchs,
R. J. Griffin, M. I. Guzman, H. Herrmann, A. Hodzic,
Y. Iinuma, J. L. Jimenez, A. Kiendler-Scharr, B. H. Lee,
D. J. Luecken, J. Mao, R. McLaren, A. Mutzel,
H. D. Osthoff, B. Ouyang, B. Piquet-Varrault, U. Platt,
H. O. T. Pye, Y. Rudich, R. H. Schwantes, M. Shiraiwa,
J. Stutz, J. A. Thornton, A. Tilgner, B. J. Williams and
R. A. Zaveri, Nitrate radicals and biogenic volatile organic
compounds: oxidation, mechanisms, and organic aerosol,
32 M. Takeuchi and N. L. Ng, Chemical composition and
hydrolysis of organic nitrate aerosol formed from hydroxyl
and nitrate radical oxidation of α-pinene and β-pinene,
33 M. A. H. Khan, M. C. Cooke, S. R. Utembe, A. T. Archibald,
R. G. Derwent, P. Xiao, C. J. Percival, M. E. Jenkin,
W. C. Morris and D. E. Shallcross, Global modeling of the
nitrate radical (NO3) for present and pre-industrial
34 S. Gross, R. Iannone, S. Xiao and A. K. Bertram, Reactive
uptake studies of NO3 and N2O5 on alkenoic acid,
alkanoate, and polyalcohol substrates to probe nighttime
aerosol chemistry, Phys. Chem. Chem. Phys., 2009, 11,
7792–7803.
35 M. D. King, K. C. Thompson and A. D. Ward, Laser Tweezer
Raman Study of Optically Trapped Aerosol Droplets of
Seawater and Oleic Acid Reacting with Ozone: Implications
Environmental Science: Atmospheres

42 S. Xiao and A. K. Bertram, Reactive uptake kinetics of NO₃ on
46 F. Sebastiani, R. A. Campbell and C. Pfrang, Ozonolysis of oleic
45 C. Pfrang, K. Rastogi, E. R. Cabrera-Martinez, A. M. Seddon,
39 C. Pfrang, F. Sebastiani, C. O. M. Lucas, M. D. King,
36 O. Vesna, S. Sjogren, E. Weingartner, V. Samburova,
33 M. W. A. Skoda, B. Thomas, M. Hagreen, F. Sebastiani and
28 R. A. Campbell, Recent advances in resolving kinetic and dynamic processes at the air/water interface using specular neutron reflectometry,Curr. Opin. Colloid Interface Sci., 2018, 37, 49–60.


