This paper is published as part of a PCCP Themed Issue on:
Physical Chemistry of Aerosols

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Received 9th March 2009, Accepted 17th July 2009
First published as an Advance Article on the web 6th August 2009
DOI: 10.1039/b904741g

Heterogeneous reactions between NO\(_3\) and N\(_2\)O\(_5\) and diethyl sebacate (DES), glycerol, oleic acid (OA), linoleic acid (LA), and conjugated linoleic acid (CLA) were studied to understand better nighttime aerosol chemistry. The reactive uptake coefficient of NO\(_3\) on the liquid alkenoic acids (OA, LA, and CLA) was found to be >0.07, which is higher than previous results for unsaturated organics, including alkenoic acids. This reaction could potentially be an important loss process of particle-phase unsaturated organic compounds in the atmosphere and in laboratory secondary organic aerosol studies. The reactive uptake coefficient of N\(_2\)O\(_5\) on liquid glycerol was also found to be relatively large with a value of \((3.2–8.5) \times 10^{-4}\), suggesting that N\(_2\)O\(_5\) heterogeneous reactions with alcohols may also be atmospherically relevant. For all measurements with OA, CLA, and DES, the reactive uptake coefficients decreased significantly upon freezing. One possible explanation is that the liquid reaction is due to both a surface reaction and a bulk reaction and that the freezing process significantly decreases the importance of any bulk reactions. NO\(_3\) reactive uptake coefficients for liquid-phase compounds decreased in magnitude in the order: alkenoic acids > DES > glycerol. This is different compared to previous gas-phase studies and the difference may be due to the large viscosity of glycerol compared to the other organic compounds studied. N\(_2\)O\(_5\) reactive uptake coefficients for liquid-phase compounds decreased in magnitude in the order: glycerol > LA > DES ≈ OA ≈ CLA.

1. Introduction

Liquid and solid aerosol particles are abundant in the troposphere, with concentrations in the range of \(10^3–10^7\) aerosol particles in 1 cm\(^3\) of ambient air. Field measurements have shown a broad variety of aerosol types, both organic and inorganic. The organic fraction comprises typically 10–90% of the total aerosol mass.\(^1\) This organic material can be in the form of pure organic particles, or alternatively the organic material can be mixed with inorganic material. In the latter case, the organic material can form organic coatings on surfaces of aqueous particles,\(^2\,3\) or organic coatings adsorbed on surfaces of solid particles, such as mineral dust.\(^4\)

The composition of this particle-phase organic material is very diverse, with hundreds to thousands of different organics identified.\(^5\,9\) Some of the classes of components in the organic aerosol fraction are alkanes, alkanoic acids, alkenoic acids, dicarboxylic acids, alcohols, and polycyclic aromatic hydrocarbons (PAH).\(^10\,12\) Sources of these organics are both biological and anthropogenic and range from terrestrial vegetation, airborne microorganisms, cigarettes, automobiles and diesel trucks, to meat cooking operations. Additionally, many particle-phase organics in the atmosphere are secondary in nature, formed from the oxidation and condensation of gas-phase precursors.

Organic particles or coatings, while in the atmosphere, experience reactions with gas-phase species that may lead to the modification of the particle or coating composition. These reactions, which are often referred to as heterogeneous reactions, are of importance for several reasons. First, they may lead to toxic or carcinogenic compounds.\(^13\) Second, they may change the hygroscopic and optical properties of organic particles, and therefore influence the ability of these particles to act as cloud condensation nuclei, to act as ice nuclei, and to scatter and absorb solar radiation.\(^13\,15\) Third, these reactions can be a major loss pathway of organic compounds in the atmosphere.\(^13\,16\) Fourth, under certain conditions, these reactions can be an important sink for gas-phase species.\(^17\) Fifth, it has been suggested that these heterogeneous reactions can lead to rapid volatilization of organic particulate matter\(^18\,20\) and are a major source of volatile organic compounds (VOC) in the atmosphere.\(^5,21\) Sixth, heterogeneous reactions may also have implications for source apportionment. Specific organic species often serve as molecular markers for probing sources of organic particles. If heterogeneous reactions change the concentrations of the selected molecular markers they can lead to errors when calculating source strengths.\(^22\)

In the following, we study heterogeneous reactions between NO\(_3\) and N\(_2\)O\(_5\) and five types of organic substrates to better understand atmospheric aerosol chemistry. The focus of these studies is to determine the reactive uptake coefficients \(\gamma\) of these gases on the different organic substrates. The reactive uptake coefficient, a parameter often used to describe a heterogeneous process, is defined as the fraction of collisions with a surface that leads to reactive loss.
\( \text{NO}_3 \) is an important nighttime oxidant in the troposphere. Concentrations of this radical range from \( <10 \text{ ppt} \) to 430 ppt.\(^7,^{23-26} \) There have only been a few studies that have explored the reactive uptake coefficient of \( \text{NO}_3 \) on organic substrates. In a pioneering study, Moise \textit{et al.}\(^{17} \) studied the reactive uptake coefficient on the following liquid and solid organics: n-hexadecane, n-octanoic acid, 1-octadecene, 1-hexadecene, heptylmethyl nonane, 1-octan0l, 7-tetradecene, conjugated linoleic acid, and nonconjugated linoleic acid. Knopf \textit{et al.}\(^{27} \) studied the reactive uptake coefficient of \( \text{NO}_3 \) on an alkane monolayer. Gross and Bertram\(^{28} \) studied the reactive uptake coefficient of \( \text{NO}_3 \) on an alkene monolayer. Gross and Bertram\(^{29} \) also studied the reactive uptake coefficient on solid PAH films. McNeill \textit{et al.}\(^{30} \) studied the \( \text{NO}_3 \) uptake coefficient on aqueous aerosols coated with a monolayer of sodium oleate. These combined studies suggest that \( \text{NO}_3 \) reactions with organics may be important in the atmosphere under certain conditions, but more work in this area is still needed to fully understand the significance of these reactions.

\( \text{N}_2\text{O}_5 \) is also an important gas-phase species during the night. It is formed from the reaction between \( \text{NO}_2 \) and \( \text{NO}_3 \) and can reach concentrations of up to approximately 10 ppb.\(^{31} \) There have only been a few studies of the reactive uptake coefficient of \( \text{N}_2\text{O}_5 \) on organics. Gross and Bertram\(^{29} \) explored the uptake coefficient of \( \text{N}_2\text{O}_5 \) on PAH surfaces and Thornton \textit{et al.}\(^{32} \) studied the uptake coefficient of \( \text{N}_2\text{O}_5 \) on solid malonic acid and azelaic acid aerosols. In addition, Lai and Finlayson-Pitts\(^{33} \) investigated the products formed from the heterogeneous reaction between \( \text{N}_2\text{O}_5 \) and 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (an unsaturated organic compound), but uptake coefficients were not reported.

We have investigated the reactive uptake of \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \) on liquid and solid organic substrates. The reactive uptake coefficients are used to assess the lifetime of these condensed-phase organics in the atmosphere. The potential importance of these reactions in laboratory studies of secondary organic aerosol (SOA) formation is also discussed.

The specific substances used for this study were diethyl sebacate (DES, \( \text{C}_{14}\text{H}_{26}\text{O}_4 \)), an alkanoate; glycerol (\( \text{C}_3\text{H}_8\text{O}_3 \)), a polyalcohol; and oleic acid (OA, \( \text{C}_{18}\text{H}_{34}\text{O}_2 \)), also known as \( \text{cis-9-octadecenoic acid} \); linoleic acid (LA, \( \text{C}_{18}\text{H}_{32}\text{O}_2 \)); and conjugated linoleic acid (CLA, \( \text{C}_{18}\text{H}_{32}\text{O}_2 \)), which is a mixture of the \( \text{cis-9}, \text{trans-11} \) and \( \text{trans-10}, \text{cis-12} \) isomers of linoleic acid. OA, LA and CLA are all alkenoic acids. Fig. 1 provides chemical structures for all organic compounds used in this study. The five organics used in this study represent different functional groups commonly found in atmospheric samples and therefore serve as models for certain organics in the atmosphere. Two of the compounds (OA and glycerol) have been observed in atmospheric field studies, and diesters of sebacic acid (decanedioic acid) have recently been used as proxies for saturated organic compounds found in the atmosphere.\(^{20,34,35} \) LA and CLA were studied to make direct comparisons between our \( \text{NO}_3 \) uptake data with those of Moise \textit{et al.}\(^{17} \).

The compounds OA, CLA, and DES have freezing points within the studied temperature range of 263–303 K. This allowed us to investigate differences in reactivity between solid and liquid films. By comparing the results for the liquid and solid compounds, we examined whether the reaction for the liquid is due to mainly a surface reaction or both a surface and a bulk reaction.\(^{17} \)

For \( \text{NO}_3 \) we find the reactive uptake on the alkenoic acid is faster than expected based on previous results for other unsaturated organics. This finding may have implications for the atmosphere and studies of SOA formation. For \( \text{N}_2\text{O}_5 \) we find that the reaction with the polyalcohol is also efficient and could potentially play an important role in atmospheric aerosol chemistry.

## 2. Experimental

### 2.1 Experimental setup and procedure

Experiments were performed in a rotating-wall flow cell coupled to a chemical ionization mass spectrometer (CIMS) described in more detail elsewhere.\(^{36} \) The rotating glass tube (1.77 cm inner diameter (I.D.), \( \sim 12 \text{ cm length} \)) fit snugly inside the flow tube. An outer tube that surrounds the flow cell allowed for temperature control to within \( \pm 1 \text{ K} \). All exposed glass and metal surfaces of the flow tube (other than the reactive surface of interest) were coated by an inert halocarbon wax or grease to avoid losses of \( \text{NO}_3 \) or \( \text{N}_2\text{O}_5 \) on these surfaces. Approximately 0.5–1 mL of the liquid organic was distributed onto the inner wall of the rotating glass cylinder. A rotation rate of approximately 10 rotations per min was used in the liquid experiments. This produced a uniform film approximately 0.5 mm thick. For conducting experiments on solid surfaces, the rotating liquid films were rapidly cooled by passing a refrigerated coolant through the outer jacket of the flow cell. The freezing temperatures (\textit{i.e.} freezing points) of each film were determined with the rotating-wall flow cell discussed above. The temperature of the flow cell was decreased at a rate of approximately 0.5 K min\(^{-1} \), and the freezing temperatures were determined visually.

Total pressures in the flow cell were 2–5 Torr and velocities in the flow cell ranged from 20–100 cm s\(^{-1} \) for the \( \text{N}_2\text{O}_5 \) experiments, and from 380–810 cm s\(^{-1} \) for the \( \text{NO}_3 \) experiments. The main carrier gas used in the experiments was He. \( \text{O}_2 \) was also added to the carrier gas to better mimic atmospheric concentrations. \( \text{O}_2 \) percentages in the flow cell ranged from 10–14\% (\( \text{NO}_3 \) experiments) to 38–54\% (\( \text{N}_2\text{O}_5 \) experiments) of the total flow. In some experiments involving LA, only He was used as a carrier gas, but no difference in measured uptake coefficient was observed compared to those experiments using a mixture of He and \( \text{O}_2 \) as a carrier. The flow was laminar in all experiments, based on the Reynolds number (\( Re < 5 \)). \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \) were added through a movable injector that allowed for varying of the reactive distance and thus the reaction time. The injector position was periodically moved during an experiment to expose an increasing surface area of the organic coating to \( \text{NO}_3 \) or \( \text{N}_2\text{O}_5 \).

\( \text{N}_2\text{O}_5 \) was generated by reacting \( \text{NO}_3 \) with an excess amount of \( \text{O}_2 \) in a flow system as described by Schott and Davidson\(^{17} \) and Cosman \textit{et al.}\(^{37} \) \( \text{NO}_3 \) was stored as solid white crystals at 197 K. \( \text{NO}_3 \) radicals were obtained by thermal conversion of gaseous \( \text{N}_2\text{O}_5 \) to \( \text{NO}_3 \) and \( \text{NO}_2 \) at 430 K in a Teflon\(^{38} \) coated...
glass oven before entering the movable injector. Due to the short residence time of the gases in the flow tube reactor (typically 20–100 ms), the recombination of NO3 and NO2 to N2O5 was negligible. N2O5 and NO3 were both detected as NO3⁻/C0 in the mass spectrometer after chemical ionization by I⁻/C0. I⁻/C0 was generated by passing a trace amount of CH3I in N₂ through a ²¹⁰Po source (NRD, model Po-2031).

N2O5 concentrations were calculated from the NO3⁻/C0 signal and the known rate constants of the reaction of N2O5 with I⁻. NO3 concentrations were estimated by assuming that all N2O5 is converted to NO3 and NO2 and approximately 20% of the NO3 thermally dissociates in the Teflon® coated glass oven based on well-known gas-phase reaction rates and modeling studies using the AcuChem chemical kinetics simulation program. Conversion of N2O5 to NO3 and NO2 in the oven was verified at the beginning of every NO3 uptake experiment by adding an excess quantity of NO to the exit of the flow tube to quantitatively convert NO3 to NO2. This conversion by NO also served as a convenient way to quantify the background signal in the NO3 experiments. The background signal was typically less than 5% of the total signal. NO3 concentrations ranged from (3.5–16) × 10¹⁰ molecules cm⁻³ and N2O5 concentrations ranged from (1–20) × 10¹¹ molecules cm⁻³. The uncertainty in these concentrations, based on the uncertainty of the rate constant for the gas-phase N2O5 + I⁻ reaction, is 40%. Observed first-order loss rate coefficients, kobs, were calculated from the depletion of the oxidant signal with increasing reaction time. Three typical plots of the natural logarithm of the NO3 signal vs. time are shown in Fig. 2 for glycerol, DES, and OA. The slopes of the
linear fits were used to determine $k_{obs}$, which was in turn corrected for concentration gradients that form close to the flow-tube wall by using the procedure developed by Brown. Uptake coefficients, $\gamma$, were calculated from the corrected $k_{obs}$ using a standard procedure. Diffusion coefficients used in these calculations were taken from Rudich et al. and Knopf et al. for NO$_3$ and N$_2$O$_5$, respectively.

As NO$_2$ is always present in our NO$_3$ experiments (due to our method of producing NO$_3$ radicals), we also measured the reactive uptake coefficients of NO$_2$ for OA, DES, and glycerol at 298 K in the presence of O$_2$. Experimental conditions were similar to the conditions discussed above. For all experiments the $\gamma$ value was at or below our detection limit ($\gamma \leq 1 \times 10^{-6}$).

### 2.2 Chemicals

Diethyl sebacate (98%), linoleic acid (≥ 99%), and conjugated linoleic acid (<1% unconjugated LA impurities) were obtained from Sigma-Aldrich; glycerol (99.9%) and oleic acid (≥ 99.0%) were purchased from Fisher-Scientific and Fluka, respectively. NO$_2$ (99.5%) was procured from Matheson. N$_2$ (99.999%), O$_2$ (99.993%), and He (99.999%) were purchased from Praxair. O$_2$ was passed through an ultraviolet light source to generate O$_3$.37,38

### 3. Results and discussion

Table 1 and Fig. 3 provide mean values of uptake coefficients for both NO$_3$ and N$_2$O$_5$ experiments at different flow cell temperatures. Typically, 5–10 experiments were performed for each heterogeneous reaction at the specified temperature. At the end of every uptake experiment, when the injector was moved to a position where the coated organic layer was no longer exposed to the oxidant flow, no release of NO$_3$ or N$_2$O$_5$ was observed. This indicates that the uptake of NO$_3$ and N$_2$O$_5$ for all organic compounds studied was irreversible.

**Table 1** Mean values of measured uptake coefficients for reactions of NO$_3$ and N$_2$O$_5$ with solid and liquid-phase organic compounds

<table>
<thead>
<tr>
<th>Surface</th>
<th>$T$/$K$</th>
<th>Phase</th>
<th>$\gamma$(NO$_3$)</th>
<th>$\gamma$(N$_2$O$_5$) $\times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OA</td>
<td>302</td>
<td>Liquid</td>
<td>0.21 ($\pm$0.79/−0.11)</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>Liquid</td>
<td>—</td>
<td>0.54 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>Liquid</td>
<td>0.18 ($\pm$0.82/−0.11)</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>Liquid</td>
<td>0.16 ($\pm$0.84/−0.06)</td>
<td>0.62 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>285</td>
<td>Liquid</td>
<td>0.17 ($\pm$0.83/−0.09)</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>283</td>
<td>Solid</td>
<td>0.053 ± 0.011</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>277</td>
<td>Solid</td>
<td>0.051 ± 0.014</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>268</td>
<td>Solid</td>
<td>0.076 ± 0.026</td>
<td>0.09 ± 0.04</td>
</tr>
<tr>
<td>DES</td>
<td>298</td>
<td>Liquid</td>
<td>(4.1 ± 0.3) × $10^{-3}$</td>
<td>0.51 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>Liquid</td>
<td>(3.6 ± 0.1) × $10^{-3}$</td>
<td>0.86 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>278</td>
<td>Liquid</td>
<td>(4.1 ± 0.5) × $10^{-3}$</td>
<td>1.30 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>272</td>
<td>Solid</td>
<td>(3.6 ± 0.5) × $10^{-4}$</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>268</td>
<td>Solid</td>
<td>0.03 ± 0.29</td>
<td>—</td>
</tr>
<tr>
<td>Glycerol</td>
<td>303</td>
<td>Liquid</td>
<td>—</td>
<td>8.14 ± 0.35</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>Liquid</td>
<td>(1.4 ± 0.3) × $10^{-3}$</td>
<td>6.45 ± 0.58</td>
</tr>
<tr>
<td></td>
<td>286</td>
<td>Liquid</td>
<td>(9.2 ± 0.4) × $10^{-4}$</td>
<td>5.11 ± 0.61</td>
</tr>
<tr>
<td></td>
<td>268</td>
<td>Liquid</td>
<td>(8.3 ± 0.5) × $10^{-4}$</td>
<td>3.98 ± 0.74</td>
</tr>
<tr>
<td>CLA</td>
<td>298</td>
<td>Liquid</td>
<td>0.37 ($\pm$0.63/−0.24)</td>
<td>0.46 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>Liquid</td>
<td>0.33 ($\pm$0.67/−0.21)</td>
<td>0.49 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>278</td>
<td>Liquid</td>
<td>0.62 ($\pm$0.38/−0.47)</td>
<td>0.39 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>Solid</td>
<td>0.08 ± 0.03</td>
<td>0.14 ± 0.13</td>
</tr>
<tr>
<td>LA</td>
<td>298</td>
<td>Liquid</td>
<td>0.29 ($\pm$0.71/−0.15)</td>
<td>1.68 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>Liquid</td>
<td>0.33 ($\pm$0.67/−0.20)</td>
<td>1.67 ± 0.30</td>
</tr>
<tr>
<td></td>
<td>278</td>
<td>Liquid</td>
<td>0.41 ($\pm$0.59/−0.27)</td>
<td>1.65 ± 0.31</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>Liquid</td>
<td>0.13 ($\pm$0.67/−0.05)</td>
<td>1.36 ± 0.14</td>
</tr>
</tbody>
</table>

* Uncertainty is calculated using a 20% uncertainty in the diffusion coefficient unless otherwise indicated.

Fig. 3 Measured reactive uptake coefficients as a function of temperature for NO$_3$ (top) and N$_2$O$_5$ (bottom) reactions on the five organic compounds studied.

The freezing temperatures for DES, OA, and CLA were (273.6 ± 1) K, (284.2 ± 1) K, and (270.3 ± 1) K, respectively. In contrast, for the studied temperature range of (263–303) K, neither the glycerol nor the LA films froze. Both remained as
supercooled liquids, even though the lowest temperatures studied were below the melting points of glycerol and LA. Melting points for OA, DES, glycerol, and LA are 287 K, 278 K, 291 K, and 268 K, respectively; the melting point for CLA was not provided by the supplier.44

3.1 Reactive uptake of NO$_3$ on the alkenoic acids OA, LA, and CLA

The uptake coefficients for all three alkenoic acids in the liquid phase were >0.07 (see Table 1). The flow tube technique used in this study is typically capable of accessing $10^{-6} < \gamma < 1$, however, for our flow rates and pressures, \( \gamma \) values greater than 0.07–0.1 (depending on the flow conditions) are greatly influenced by gas-phase diffusion to the reactive surface. In this case, a small uncertainty in the observed first-order rate constant (\( k_{obs} \)), or the diffusion coefficient, results in a large uncertainty in the reactive uptake coefficients.

Average uptake coefficients for the frozen alkenoic acids OA and CLA were approximately 65% and 80% lower, respectively, than the corresponding liquid-phase data. This suggests that the net liquid-phase reaction may be a combination of both a surface reaction and a bulk reaction, since the freezing process is expected to greatly decrease the importance of any bulk reactions in our experiments. Alternatively, the reactive uptake for both the liquid- and solid-phase experiments might only be due to surface reactions, where the liquid-phase surface is much more favourable for uptake and reactivity.45 In these experiments, we cannot discern between the two different possibilities. We assume the former until further information is available.

For all the liquids studied, the NO$_3$ loss was constant with time, which was expected since the surface was continuously being replenished by the rotation of the liquid film. Furthermore, for all frozen surfaces studied, NO$_3$ loss was also constant with time, and there was no indication of “chemical aging” of the surface due to a decrease in reactive surface products that continuously creates a “fresh” unreacted surface. Alternatively, there could be some mobility on the frozen surface and reactants may diffuse into the bulk and react with subsurface molecules.17

The reactive uptake for the liquid (and most likely also for the solid) is due to the addition of the NO$_3$ radical to a C=C bond, based on recent product studies for NO$_3$ reactions with liquid OA particles46,47 and a study of NO$_3$ reactivity on a terminal alkene monolayer.28 Results from these product studies have indicated that the likely mechanism involves the addition of the NO$_3$ radical to the C=C bond to form a C-ONO$_2$ functional group at one C atom and an alkyl radical at the other C atom. O$_2$ can be added to the radical to form a peroxy radical (ROO$^*$), which can then undergo a series of radical reactions to form products such as carboxyls, alcohols, nitrites, or peroxy-nitrates.46,47

In Table 2, \( \gamma \) values for alkenoic acids are compared with \( \gamma \) values determined in other studies using unsaturated organic substrates. Moise et al.17 used a coated-wall flow tube reactor to study both liquid and frozen unsaturated organics, including LA and CLA. Our data for LA and CLA are larger than the results from Moise et al., even if one considers the uncertainty in the measurements. Another difference between our results and the results from Moise et al.17 for alkenoic acids are the changes observed upon freezing the liquid. As mentioned above, we observed a decrease in the reactive uptake coefficient when freezing the liquid. In contrast, Moise et al. reported that the change in values of \( \gamma \) upon freezing of liquid alkenoic acids was within the experimental uncertainty, although Moise et al. reported that the uptake coefficients of NO$_3$ by n-hexadecane and n-octanoic acid decreased by a factor of 5 upon freezing. This behavior was explained by reactions occurring in the bulk of the organic liquid as well as on the surface for n-hexadecane and n-octanoic acid. It is also interesting to note that unlike the results for unsaturated organics, our results for saturated organics are in good agreement with the results from Moise et al.17 (see section 3.3).

Also shown in Table 2 is preliminary data by Ziemann et al.38 These authors used an environmental chamber to determine the reactive uptake coefficient of NO$_3$ on liquid OA aerosols at room temperature, and they obtained results consistent with our findings.

Both our experiments and the experiments by Moise et al. were performed with a rotating-wall flow reactor, experimental conditions such as pressure and temperatures were similar, and both experimental apparatuses were validated by studying known gas-phase reactions. Moise et al.17 studied the gas-phase reaction of 1-butene with NO$_3$ and obtained rate constants consistent with literature values. We measured the second order rate constant for the gas-phase reaction of NO$_3$ with NO at room temperature using our flow cell. We obtained \( (2.96 \pm 0.15) \times 10^{-11} \) cm$^3$ molecule$^{-1}$ s$^{-1}$ which agrees well with established literature values in the range of \((2.4–3.0) \times 10^{-11} \) cm$^3$ molecule$^{-1}$ s$^{-1}$7,49,50

One experimental parameter that differs between our studies and those by Moise et al.17 is the NO$_3$ concentration range. Moise et al. used \((0.5–5) \times 10^{13} \) molecules cm$^{-3}$, a range that is slightly above that of \((3.5–16) \times 10^{10} \) molecules cm$^{-3}$ used in our investigation. It is, however, unlikely that this can entirely explain the discrepancies between data sets. Our recent results suggest a potential uncertainty in the reactive uptake coefficients for NO$_3$-unsaturated organic reactions. More studies are needed to resolve the apparent discrepancies between the two data sets.

McNeill et al. studied the uptake of NO$_3$ on aqueous particles coated with a monolayer of sodium oleate and obtained a value of \(<10^{-3} \) cm$^3$ molecule$^{-1}$ s$^{-1}$ This study is more similar to studies on frozen films where only the surface or top few layers were accessible. For frozen films, the \( \gamma \) values obtained in this study are at least 40 times greater than those obtained by McNeill et al. These differences in reactive uptake coefficients could be rationalized by differences in surface-film structure. A monolayer only has one layer available for reaction whereas in frozen films several top layers are potentially accessible. Frozen films are also expected to have surface defects such as steps and kinks that may enhance reactivity.
Table 2  Comparison of uptake coefficient data for the reaction of NO3 on liquid and solid surfaces of saturated and unsaturated organics

<table>
<thead>
<tr>
<th>Surface</th>
<th>Liquid surface</th>
<th>Solid surface</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T/K</td>
<td>8liquid</td>
<td>T/K</td>
</tr>
<tr>
<td>Saturated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DES</td>
<td>278–298</td>
<td>(3.5–4.5) × 10^{-3}</td>
<td>263–272 (2.3–4.1) × 10^{-4}</td>
</tr>
<tr>
<td>α-Hexadecane</td>
<td>293</td>
<td>(2.6 ± 0.8) × 10^{-3}</td>
<td>283–289 (3.8 ± 1.0) × 10^{-4}</td>
</tr>
<tr>
<td>Heptamethyl nonane</td>
<td>253</td>
<td>(2.1 ± 0.8) × 10^{-3}</td>
<td>234 (2.6 ± 0.9) × 10^{-3}</td>
</tr>
<tr>
<td>Unsaturated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OA</td>
<td>285–302</td>
<td>≥ 0.07</td>
<td>268–283 (3.8–10) × 10^{-2}</td>
</tr>
<tr>
<td>LA</td>
<td>298</td>
<td>0.13 ± 0.02</td>
<td>—</td>
</tr>
<tr>
<td>CLA</td>
<td>288</td>
<td>≥ 0.13</td>
<td>—</td>
</tr>
<tr>
<td>1-Hexadecene</td>
<td>288</td>
<td>(1.5 ± 0.2) × 10^{-2}</td>
<td>248–263 (1.1 ± 1.3) × 10^{-2}</td>
</tr>
<tr>
<td>1-Octadecene</td>
<td>278–298</td>
<td>≥ 0.12</td>
<td>263 ± 0.08 ± 0.03</td>
</tr>
<tr>
<td>7-Tetradecene</td>
<td>273</td>
<td>(7.9 ± 1.2) × 10^{-3}</td>
<td>253–263 (7.8 ± 1.4) × 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>277</td>
<td>(2.3 ± 0.9) × 10^{-3}</td>
<td>254–274 (1.8 ± 0.3) × 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>(1.6 ± 0.3) × 10^{-5}</td>
<td>283 (1.4 ± 0.1) × 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>246</td>
<td>(5.8 ± 2.0) × 10^{-5}</td>
<td>283 (5.2 ± 2.0) × 10^{-3}</td>
</tr>
</tbody>
</table>

a Unpublished data.

3.2 Reactive uptake of NO3 on glycerol

The films of glycerol did not freeze for the temperature range studied but rather became a supercooled liquid at the lowest temperatures studied (well below the literature melting point of glycerol). The uptake coefficients measured for liquid glycerol were in the range of (7.8–17) × 10^{-4} (which includes measurement uncertainty).

There has only been one previous study of the reactive uptake coefficient of NO3 on a liquid-phase saturated alcohol. Moise et al.17 studied 1-octadecanol and obtained a value of 7.1 × 10^{-3} for the liquid. The mechanism for the NO3 reaction with the alcohol, based on gas-phase reactions, likely involves hydrogen abstraction.17,51,52 However, product studies are needed to confirm the reaction mechanism.

3.3 Reactive uptake of NO3 on DES

The uptake coefficients measured for liquid DES were (3.5–4.6) × 10^{-3} (this range includes measurement uncertainties). Freezing of DES resulted in a decrease of γ of about one order of magnitude. This suggests that the reactive uptake of NO3 on the liquid is due to both a surface and a bulk process.

There are no previous studies of NO3 reactive uptake on liquid or solid alkanoates available for comparison. Gas-phase measurements suggest the reaction rates for saturated esters are similar to those for saturated hydrocarbons.53 Thus, the presence of the ester functional group does not significantly affect the reactivity of the alkyl chain. Table 2 provides a comparison of our results for the alkanoate with previous measurements of the uptake of NO3 with solid and liquid alkanes by Moise et al.17 In this case, our results for the alkanoate DES are in reasonable agreement with the measurements by Moise et al. Considering gas-phase reactions between NO3 and alkanoates, the mechanism is probably due to abstraction of an H atom, similar to the glycerol + NO3 mechanism but product studies are needed to lend credence to this hypothesis.

3.4 Overall trend in NO3 reactivity

For the solid surfaces studied, the trend in the reactive uptake coefficient is alkenoic acid > alkanoate. This trend is consistent with the trend observed for gas-phase reactivity, assuming the alkenoic acid reactivity is due to the C–C bond (a reasonable assumption based on recent product studies).46,47 For example, the gas-phase reaction rate coefficients for propene and methyl propionate are 9.5 × 10^{-15} cm^3 molecule^{-1} s^{-1}, and <3.3 × 10^{-17} cm^3 molecule^{-1} s^{-1}, respectively.53,54

The trend in reactive uptake coefficients for the liquids is alkenoic acid > alkanoate > polyol. This is different from the gas-phase reactivity trend, which is alkenoic acid > alcohol > alkanoate (again assuming the alkenic acid reactivity is due to the C–C bond). For example, the gas-phase reaction rate coefficient for propanol is 1.5 × 10^{-15} cm^3 molecule^{-1} s^{-1}, which is between the rate coefficient for propene and methyl propionate.54 (Although, keep in mind that the data on gas-phase reactivity for alkanoates is very limited.) For the liquid, the reactive uptake coefficient of glycerol is lower than expected based on gas-phase reactivity. For a possible explanation, we used the resistor model of gas-liquid interactions55 and assumed that for all liquids the reaction occurs mainly in the bulk (since γ values for experiments with frozen DES, OA, and CLA were significantly lower than for the corresponding liquid experiments). If the reaction occurs in the bulk, the reactive uptake coefficient can be explained with the following equation:

\[
\gamma = \frac{1}{\gamma_{rxn}} = \frac{1}{z} + \frac{c_{avg}}{4HRT\sqrt{Dk_{rxn}}} \tag{1}
\]

where z is the probability that a molecule that strikes the surface enters the bulk, \( c_{avg} \) is the mean molecular velocity of NO3, H is the Henry’s law solubility constant, R is the gas constant, T is the temperature, D is the diffusion coefficient for NO3 in the organic liquid, and \( k_{rxn} \) is the first-order rate constant for reaction in the liquid.

Eqn (1) shows that the reactive uptake coefficient is a function of the bulk-phase rate coefficient (\( k_{rxn} \)), the Henry’s law solubility, and the diffusion coefficient of NO3 in the liquid. It is interesting to note that the viscosity of liquid glycerol is more than an order of magnitude higher than that of liquid OA or liquid DES (viscosity data for LA and CLA are not available, to our knowledge). Viscosities at 293–298 K
for glycerol, OA, and DES are 1500 mPa s, 64 3.8 mPa s, and 5.88 mPa s, respectively. The diffusion coefficient of a species in a liquid is related to the viscosity through the Stokes–Einstein equation:

\[ D = \frac{kT}{6\pi\eta r} \]  

(2)

where \( D \) is the diffusion coefficient, \( k \) is the Boltzmann constant, \( T \) is the temperature, \( \eta \) is the viscosity of the liquid, and \( r \) is the radius of the diffusing species. Eqn (2) and the liquid viscosity data suggest that the diffusion coefficient of NO\(_3\) is more than an order of magnitude smaller in glycerol than OA and DES. This information together with eqn (1) leads us to hypothesize that the NO\(_3\)--glycerol reactive uptake coefficient is lower than the NO\(_3\)--DES reactive uptake coefficient because of the small diffusion coefficient of NO\(_3\) in liquid glycerol [ultimately resulting in a smaller \( H(Dk_{\text{rxn}})^{0.5} \) value for eqn (1)]. Measurements of reactive uptake coefficients on different alcohols with different viscosities may provide an adequate data set for resolving this discrepancy.

### 3.5 Reactive uptake of NO\(_3\) on glycerol

For all organic compounds studied, the NO\(_3\) reactive uptake coefficient was the largest on glycerol. Uptake coefficients ranged from (3.2–8.5) \times 10^{-5} (range incorporates uncertainties in the measurements). Our studies are the first measurements of the reactive uptake coefficients of NO\(_3\) on condensed-phase alcohols. However, reactions between NO\(_3\) and saturated alcohols have been observed in the gas phase.\(^{51,52}\) In addition, the condensed-phase reaction between NO\(_3\) and saturated alcohols is known to produce organonitrates.\(^{59}\) The mechanism for the NO\(_3\) reaction with an alcohol has been suggested to occur via a six-membered ring, leading to an organic nitrate and HNO\(_3\).\(^{51}\) The suggested mechanism is shown in Fig. 4.

### 3.6 Reactive uptake of NO\(_3\) on the alkenoic acids OA, LA, and CLA

For the alkenoic acids, liquid-phase reactions with NO\(_3\) yielded reactive uptake coefficients in the range of (3.7–19.7) \times 10^{-5}. Solid-phase reactions of OA and CLA with NO\(_3\) gave \( \gamma \approx 3 \times 10^{-5} \). The decrease in \( \gamma \) below the freezing point suggests that the reaction for the liquid was due to a combination of surface and bulk reactions. For all NO\(_3\) studies on both liquid and solid films, the loss of NO\(_3\) was constant over time, similar to the NO\(_3\) experiments.

There have been no previous studies of the reactive uptake coefficients of NO\(_3\) on a liquid or solid alkenoic acid. However, Lai and Finlayson-Pitts studied the heterogeneous reaction between NO\(_3\) and 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (an unsaturated organic compound) on the inside surface of a glass reaction cell, but uptake coefficients were not reported.\(^{35}\) Major products identified in this previous study included molecules with nitro and nitrate functional groups. The initial step in the reaction mechanism was thought to be direct reaction of NO\(_3\) with the double bond leading to a nitronitrile which can undergo subsequent reactions. This was consistent with an early study by Stevens and Emmons.\(^{60}\)

### 3.7 Reactive uptake of NO\(_3\) on DES

Reactive uptake coefficients determined for liquid DES were in the range of (4.3–14) \times 10^{-5} and were \(<6 \times 10^{-6}\) for the solid. As \( \gamma \) dropped significantly upon freezing, this again suggests that reaction on the liquid occurs both at the surface and in the bulk.

As shown in Fig. 3, a significant negative temperature dependence was observed for liquid DES. To explain this trend we again use the resistor model and eqn (1), which assume the reaction for the liquid occurs mainly in the bulk. Diffusion coefficients and rate constants typically show a positive temperature dependence. Increasing either \( D \) or \( k_{\text{rxn}} \) would lead to higher results for \( \gamma \) and cannot explain the negative temperature dependence for DES with NO\(_3\). The mean molecular velocity, \( c_{\text{avg}} \), also has a positive temperature dependence and therefore leads to a negative temperature dependence for \( \gamma \). However, increasing the temperature from 278 K to 298 K increases \( c_{\text{avg}} \) by only 3.5%, while the value of \( \gamma \) for the DES + NO\(_3\) reaction decreased by a factor of 2.6 over this temperature range. Therefore the observed temperature dependence cannot be due to changes in the molecular velocity. \( H \), Henry’s law solubility constant, also has a negative temperature dependence\(^{32}\) and we therefore assume that the observed increase in \( \gamma \) at lower temperatures is due to the higher solubility of NO\(_3\) in the liquid, leading to more NO\(_3\) in the liquid bulk and thus a higher probability of reactive uptake.

There have been no previous studies of NO\(_3\) on liquid or solid alkanotes for comparison. Also, we are not aware of any gas-phase reactions between NO\(_3\) and alkanotes. The only other NO\(_3\) heterogeneous study for pure saturated organics that we are aware of is a study by Thornton \textit{et al.}\(^{32}\) These authors measured the uptake of NO\(_3\) on solid malonic acid and azelaic acid aerosols and determined uptake coefficients to be \(<10^{-7}\) and (5 ± 3) \times 10^{-4}, respectively. The values they obtained for azelaic acid are slightly higher than our result for DES, but the difference may also be due to the presence of water in the experiments by Thornton \textit{et al.}\(^{32}\) The relative humidity (RH) used in the azelaic acid experiments by Thornton \textit{et al.} was 85% humidity, whereas we had a dry carrier gas.

Others have also studied the reactive uptake coefficient of NO\(_3\) on aqueous organic particles, but we have not included this in the discussion, since the reactivity in these experiments was most likely due to the hydrolysis reaction of
N₂O₅ and not a reaction between N₂O₃ and the organic compound.⁴⁻¹⁻⁶⁻⁶³

3.8 Overall trend in N₂O₅ reactivity

The trend in the reactive uptake coefficients for the three frozen organic compounds in reaction with N₂O₅ is CLA > OA > DES. N₂O₅ uptake coefficients for the liquid organic compounds studied at 298 K are in the order: glycerol > LA > DES ≈ OA ≈ CLA. There is very little data on N₂O₅-organic gas-phase reactions for comparison. However, a recent study by Pfrang et al.⁶⁴ provides insight into the relative reactivity of an OH functional group vs. a double bond. These authors studied the reaction between N₂O₅ and pentenols and the identified products were mainly unsaturated nitrates. These gas-phase results suggest that the OH functional group is more reactive than the double bond toward N₂O₅, which is consistent with our liquid-phase uptake results.

4. Atmospheric implications

4.1 Oxidation lifetimes for single component liquid organic particles

To determine if the reactions we investigated in this study are important in the atmosphere, we calculated the oxidation time scale from our experimental data and compared this time scale with the atmospheric residence time of the aerosol particles. This analysis is similar to the analysis recently used by Robinson et al.²² to determine the effect of OH and O₃ reactions on the molecular composition of organic aerosols in the regional context. Following Robinson et al., we calculated the oxidation lifetime using the following equation:

\[ \tau_{\text{liquid}} = \frac{N_{\text{tot}}}{\Phi} = \frac{4N_{A}rp}{3M_{cav}\bar{v}_{\text{avg}}[\text{ox}]} \]  

(3)

where \( \tau_{\text{liquid}} \) is the oxidation lifetime of a single-component liquid particle, \( N_{\text{tot}} \) is the total number of organic molecules in the particle, \( \Phi \) is the flux of oxidant into the particle, \( r \) is the particle radius, \( \rho \) is the particle density (assumed to be the density of the pure liquid), \( N_{A} \) is Avogadro’s number, \( M \) is the molecular weight of the organic molecule, \( \gamma \) is the reactive uptake coefficient, \([\text{ox}]\) is the concentration of the gas-phase oxidant, and \( \bar{v}_{\text{avg}} \) is the average velocity of the oxidant in the gas phase.²² This time scale was derived by setting the total number of oxidation events equal to the initial number of molecules in the particles.²² This simple calculation gives an estimate for the time needed for all the molecules in the particles to be oxidized.

We carried out these calculations for OA, DES, and glycerol using NO₃, N₂O₅, and OH as the oxidants (OH calculations were performed for sake of comparison). Oxidant mixing ratios used in the calculations were 25 ppt for NO₃, 1 ppt for N₂O₅ and 0.06 ppt for OH (all 24 h averages). NO₃ and N₂O₅ concentrations used in these experiments roughly correspond to moderate pollution levels.⁶⁵ It should be noted, however, that tropospheric NO₃ and N₂O₅ mixing ratios are highly variable. For example, recent measurements by Penkett et al.⁶⁶ over western Europe suggest an average NO₃ mixing ratio of 350 ppt, and aircraft measurements by Brown et al. indicate NO₃ mixing ratios of up to several hundred ppt in the boundary layer over north eastern USA.⁶⁶ OH concentrations used in these calculations correspond roughly to summer conditions in an urban environment.⁶⁶,⁶⁸

The results of these calculations are shown in Fig. 5 as a function of particle size. For reference, the size of organic particles in the atmosphere can range from a few nanometres to approximately 10 μm, depending on the source and environment. In an urban environment the mass median diameter for particles in the accumulation mode is typically between 0.2–0.6 μm.⁷²,⁶⁹ Global 3D models of ²¹⁰Pb and carbonaceous aerosols suggest aerosol residence times of 5–15 days,⁷⁰,⁷¹ while radioactive tracer measurements suggest an atmospheric residence time of the order of 10 days for some regions influenced by pollution.⁷² In Fig. 5 we have indicated

Fig. 5 Atmospheric lifetimes, \( \tau \), of liquid droplets as a function of particle diameter during oxidations by NO₃, N₂O₅, or OH at 298 K. It is assumed that the whole particle consists of OA (a), DES (b) or glycerol (c). For NO₃ and N₂O₅, reactive uptake coefficients determined in this study were used for liquids at approximately 298 K. For the reaction of OA with NO₃, a reactive uptake coefficient of 0.5 was chosen. For OH, a reactive uptake coefficient of 0.5 was assumed for all substrates.⁸⁴
times of 5 and 15 days with horizontal lines to allow for easier comparison.

Fig. 5a shows that the NO₃ oxidation lifetime for OA-like particles is short compared to aerosol particle residence times. Even for N₂O₅, the oxidation lifetime is comparable to the residence time of atmospheric aerosols. The predicted short lifetimes of OA shown in Fig. 5 are in contrast to field measurements together with source fluxes that suggest lifetimes of OA are of the order of days.²²,⁷³ One possible explanation for this discrepancy is a difference in the phase (i.e. liquid vs. solid vs. semi-solid) between the substrates investigated in our work and the OA-containing particles in the atmosphere.³⁶,⁷⁴–⁸⁰ One of the main sources of OA in the atmosphere is meat cooking operations. The phase behaviour for these multicomponent particles is not well understood, but based on thermodynamic arguments, these particles are likely to be solid–liquid mixtures.³⁶ In solid–liquid mixtures, the lifetime of OA can be much longer due to trapping of the OA in or by the solid structure. This has been shown previously for O₃ reactions with OA-containing particles.³⁶,⁷⁴–⁸⁰ Other possible explanations for the differences between the laboratory studies and the field measurements are differences in diffusion and solubility of NO₃ in pure OA, compared to OA-containing particles in the atmosphere.⁷⁴,⁷⁵,⁸¹ Note that although meat cooking aerosols are likely to be solid–liquid mixtures, a majority of organic particles in the atmosphere are likely to be liquid, since for most aerosols the concentration of any specific organic is small.⁸²

Fig. 5b shows the oxidation lifetime of DES particles. For NO₃ and N₂O₅ heterogeneous reactions, the oxidation lifetime is comparable (or shorter) than the residence time of aerosol particles in the atmosphere. Also, the oxidation lifetime associated with NO₃ is comparable to the oxidation lifetime associated with OH.

Fig. 5c shows the oxidation lifetime of glycerol particles. The oxidation lifetime associated with N₂O₅ heterogeneous reactions is short compared to the residence time of aerosol particles. Glycerol has three OH groups which probably enhance its reactivity compared to alcohols which contain only one OH group. Studies of the reactive uptake coefficient of N₂O₅ on other alcohols (i.e. diols or compounds with a single OH group) would be interesting.

The results in Fig. 5 were calculated for three specific organic compounds. In addition, the results correspond to single-component organic aerosols. Atmospheric aerosols are complex mixtures containing multiple components. Nevertheless, the present results are important first outcomes for understanding the importance of these heterogeneous reactions and provide a “back-of-the-envelope estimate” for the lifetime of condensed phase organics in the atmosphere.

In the future, measurements and calculations involving more complex aerosols (which are better models for atmospheric aerosols) will be required. Also, the apparent discrepancies between our work and the work by Moise et al.¹⁷ need to be resolved. However, until more data is available, the results shown in Fig. 5 may be useful for estimating the importance of NO₃ and N₂O₅ on the lifetime of organic species in atmospheric aerosols.

4.2 Importance of these heterogeneous reactions to secondary organic aerosol (SOA) studies

One area where these heterogeneous reactions may be important is in SOA experiments with NO₃ radicals. In these studies, NO₃ heterogeneous reactions may occur during secondary organic aerosol formation and aging. To illustrate this point we refer to a recent SOA study by Ng et al.⁸³ These authors studied the SOA formation from reactions of isoprene with nitrate radicals using NO₃ concentrations of approximately 140 ppt. These authors proposed that heterogeneous reactions may have been important in their studies. Here we use our new reactive uptake results to support this suggestion.

We assume here that in general SOA particles are liquid and the results from our studies are applicable to particles generated in SOA studies. This, of course, needs to be verified in future studies, but this analysis is still insightful for estimating the importance of NO₃ heterogeneous chemistry in SOA laboratory experiments.

To estimate if NO₃ heterogeneous reactions may be important in the SOA studies by Ng et al.⁸³ we calculate the oxidation lifetime of unsaturated organic molecules and saturated organic molecules in the condensed-phase using eqn (3), with a particle diameter of 200 nm and [NO₃] = 140 ppt. For the calculations of the oxidation lifetime of the unsaturated and saturated organics we used the reactive uptake coefficients for OA and DES determined in our studies, respectively. Using eqn (3) resulted in oxidation lifetimes of 7.6 min and 18.2 h for unsaturated and saturated organics, respectively. The experiment length used by Ng et al. was approximately 1–2 h, so heterogeneous reactions between NO₃ and saturated organics likely did not play an important role (at least not based on our DES reactive uptake coefficients). However, for the unsaturated compounds, the oxidation lifetime is much shorter than the experiment length, suggesting heterogeneous reactions may have been important. Unsaturated organics were suggested products of the SOA chemistry, according to Ng et al. These authors have also suggested that the unsaturated organics may have partitioned into the condensed phase and reacted through heterogeneous chemistry. Our results and calculations above provide support for the latter suggestion.

In SOA studies with NO₃, N₂O₅ is often used as the source and N₂O₅ concentrations are higher than NO₃. As a result, N₂O₅ heterogeneous reactions are potentially important in some of these studies as well. Considering our reactive uptake coefficient results for alkenoic acids and DES, N₂O₅ concentrations would need to be roughly 500 ppb in order for N₂O₅ heterogeneous reactions with unsaturated and saturated organics to be important in SOA studies lasting approximately 1 h (which is roughly the time scale of some chamber experiments). However, if the results for glycerol are applicable to SOA studies, N₂O₅ heterogeneous chemistry will be important at even lower N₂O₅ concentrations.

Again, these calculations correspond to single-component organic aerosols. SOA aerosols are also complex mixtures containing multiple components. In the future, measurements and calculations involving more complex aerosols (which are better models for SOA) will be required.
Table 3  Estimated atmospheric lifetimes, $\tau$, for solid OA and DES surfaces in reactions with NO$_3$, N$_2$O$_5$, and OH

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Mixing ratio</th>
<th>OA $\gamma$</th>
<th>OA $\tau$</th>
<th>DES $\gamma$</th>
<th>DES $\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3$</td>
<td>25 ppt</td>
<td>0.06$^a$</td>
<td>5.8 min</td>
<td>3.6 x 10$^{-4}$</td>
<td>16.2 h</td>
</tr>
<tr>
<td>N$_2$O$_5$</td>
<td>1 ppb</td>
<td>9.4 x 10$^{-6}$</td>
<td>20.4 h</td>
<td>3.4 x 10$^{-6}$</td>
<td>2.4 d</td>
</tr>
<tr>
<td>OH</td>
<td>0.06 ppt</td>
<td>0.5$^b$</td>
<td>2.5 h</td>
<td>0.5$^b$</td>
<td>2.5 h</td>
</tr>
</tbody>
</table>

$a$ $\gamma$ value obtained from this study. $^b$ Assumed $\gamma$ value based on a previous study of OH reactivity.$^{84}$

4.3 Oxidation time scale for surface organics

To calculate the oxidation time scale for a solid organic surface under atmospheric conditions, the following equation$^{16,29}$ was used:

$$\tau_{\text{solid}} = \frac{4N_{\text{tot}}}{\gamma c_{\text{avg}}[Ox]}$$  (4)

where $\tau_{\text{solid}}$ is the oxidation lifetime of a solid surface (i.e. the time needed for 63% of the surface molecules to be oxidized) and $N_{\text{tot}}$ is the number of organic molecules on the surface. For these calculations we used $\gamma$ values determined from heterogeneous reactions of solid organic surfaces and an $N_{\text{tot}}$ value of 1 x 10$^{14}$ molecules cm$^{-2}$. Calculations were performed for both OA and DES. The same oxidant concentrations used in section 4.1 were used in eqn (4).

The results for these calculations are shown in Table 3. The trends are similar to the trends observed for the liquid, but the oxidation time scales are shorter since, in this case, only the surface is oxidized. Recently, Moise and Rudich$^{16}$ carried out a similar analysis for NO$_3$ and OH to determine the processing time for an organic coated aerosol. Their time scales were similar to ours except for NO$_3$ with a solid unsaturated organic, since our measured reactive uptake coefficients for a solid unsaturated organic are larger than the values used by Moise and Rudich.

Eqn (4) was derived by assuming that the reaction probability is proportional to the fraction of unreacted surface sites. This is a simple expression for estimating the lifetime of surface organics and has been used in previous studies to calculate the surface lifetime of organic molecules. Recently it has been shown that many atmospheric cases fit a Langmuir–Hinshelwood mechanism.$^{84,85}$ At this point, an analysis involving a Langmuir–Hinshelwood mechanism (which should be more accurate) is not possible since the parameters necessary for describing these heterogeneous reactions with the Langmuir–Hinshelwood mechanism are not known. Nevertheless, our calculations are important first outcomes for assessing the importance of these heterogeneous reactions.

4.4 Fates of NO$_3$ and N$_2$O$_5$

Above, we discussed the fate of particle-phase organics. Here, we discuss the fate of NO$_3$ and N$_2$O$_5$ based on the modeling study by Moise et al.$^{17}$ These authors used a box model to study the effect of NO$_3$–organic heterogeneous reactions on gas-phase [NO$_3$] (defined as [NO$_3$] + [N$_2$O$_5$]). Using $\gamma_{\text{NO}_3} = 3 \times 10^{-3}$, they observed a decrease in [NO$_3$] of ~10% for certain atmospheric conditions. Increasing $\gamma_{\text{NO}_3}$ to 1 x 10$^{-2}$ resulted in a 26% decrease of [NO$_3$] for certain conditions. A reactive uptake coefficient for NO$_3$ of 1 x 10$^{-2}$ is more consistent with our experimental results for unsaturated organic compounds. However, since the uptake of NO$_3$ for unsaturated organics is large, these molecules should be rapidly oxidized in the atmosphere (unless matrix effects play a role). In this case, the large uptake coefficients will only be important close to emission sources and only if there is a large source of aerosol unsaturated organics. Thomas et al. reached a similar conclusion when modeling O$_3$ heterogeneous reactions with particle-phase unsaturated organics.$^{86}$

5. Conclusions

Laboratory studies of the reactive uptake coefficient ($\gamma$) for heterogeneous reactions between NO$_3$ and N$_2$O$_5$ and five different organic compounds were conducted to better understand the atmospheric importance of these reactions. The specific substances used for this study contain functional groups commonly found in atmospheric samples of aerosol particles and may thus aid in the interpretations of certain organic compounds in the atmosphere. This study adds important $\gamma$ values to a relatively small set of data and highlights a potential uncertainty in NO$_3$–alkenoic acid heterogeneous reactions.

The reactive uptake coefficients were used to show that NO$_3$ heterogeneous reactions with liquid-phase unsaturated and saturated organics may be important in the atmosphere and that N$_2$O$_5$ heterogeneous reactions with alcohols could also be important. Experimental data also suggests that NO$_3$ and N$_2$O$_5$ heterogeneous reactions could be important in some secondary organic aerosol (SOA) studies.

Measurements and calculations were carried out for single-component organic aerosols and substrates. These results are important first outcomes for understanding the importance of these heterogeneous reactions and provide a “back-of-the-envelope estimate” for the lifetime of condensed phase organics in the atmosphere. However, atmospheric aerosols are complex mixtures. In the future, measurements and calculations involving more complex aerosols will be required. Until further studies have been conducted, the results contained herein will be useful for estimates of at least an upper limit on the influence of NO$_3$ and N$_2$O$_5$ on lifetimes of organic species in atmospheric aerosols.

Acknowledgements

The authors would like to acknowledge financial support from the Natural Science and Engineering Research Council of Canada (NSERC) and the Canada Research Chair Program. We also thank P. J. Ziemann and P. Campuzano-Jost for several helpful discussions regarding material related to the manuscript.

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