Abstract

Atmospheric heterogeneous reaction could modify the physical properties and chemical composition of aerosol particles, thereby affecting their roles in climate, air pollution, and human health. The current knowledge of heterogeneous reactions between nighttime gas-phase oxidants and organic aerosols is very limited. The goal of this thesis was to contribute to the understanding of such reactions, particularly to the kinetics of NO$_3$ and N$_2$O$_5$ reactions with a variety of organic substrates and mixtures that can serve as proxies for aerosol particles.

In the first series of studies, we investigated the reactive uptake of NO$_3$ with binary organic mixtures of an unsaturated organic (methyl oleate) and saturated molecules as “matrix molecules”. For liquid mixtures, the uptake coefficients ($\gamma$) of the matrices were significantly increased with the addition of small amounts of methyl oleate. The increase can vary by a factor of 5 depending on the type of matrix used. For solid-liquid mixtures, the uptake coefficient decreased by a factor of 10 after exposure to NO$_3$ for 90 minutes. For all liquid mixtures, the atmospheric lifetime was estimated on the order of a few minutes (with an upper limit of 35 mins), whereas, for liquid-solid mixtures, a lower limit to the lifetime was estimated to be 1-2 hours.

In the second series of studies, we investigated NO$_3$ uptake on solid tridecanal and the uptake on liquid binary mixtures containing tridecanal and saturated organics as matrices. Uptake on the solid tridecanal was shown to be efficient, with $\gamma = (1.6 \pm 0.8) \times 10^{-2}$. For liquid binary mixtures, the uptake coefficient also depended on the matrix molecule. The atmospheric lifetime of aldehydes was estimated to range from 1.9–7.5 h due to NO$_3$ oxidation.

In the third series of studies, we investigated the N$_2$O$_5$ uptake kinetics on alcohols. The uptake coefficients of N$_2$O$_5$ for five different alcohols at 293 K varied by 2 orders of magnitude, ranging from $3 \times 10^{-4}$ to $1.8 \times 10^{-2}$. The atmospheric lifetime of alcohols was calculated to range from 0.6–130 h, depending on the physical and chemical properties of the organic liquid.
Preface

Chapter 3 (Paper has been submitted to PCCP as first author status: S. Xiao and A.K. Bertram, Reactive Uptake Kinetics of NO$_3^-$ on Multicomponent and Multiphase Organic Mixtures Containing Unsaturated and Saturated Organics.)

- identified research question with help from supervisor
- performed all the uptake measurements of NO$_3^-$ with the pure organics and the mixtures
- performed all the DSC measurements
- prepared all figures and tables for the manuscript
- shared manuscript preparation with my supervisor

Chapter 4 (Paper to be submitted as second author status: R. Iannone, S. Xiao, and A.K. Bertram, Potentially Important Nighttime Heterogeneous Chemistry: NO$_3^-$ with Aldehydes and N$_2$O$_5$ with Alcohols.)

- identified research question with help from supervisor
- performed all the uptake measurements of N$_2$O$_5$
- performed about half of the uptake measurements of NO$_3^-$ with tridecanal mixtures
- prepared all figures and tables for the manuscript
- shared duties in manuscript preparation with Richard Iannone and the supervisor
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1 Introduction to Atmospheric Aerosols and Heterogeneous Atmospheric Reactions

1.1. Introduction to Atmospheric Aerosols

Aerosols are generally defined as relatively stable suspensions of solid and liquid particles in a gas. In the atmospheric sciences, aerosols are typically referred to as particulate matter with diameters between 0.002–100 μm (where the lower limit comprises clusters and the upper limit comprises particles that rapid sediment in the atmosphere). The upper size limit of interest in atmospheric chemistry is usually 10 μm. The atmosphere contains significant concentrations of aerosols, typically in the range of $10^2$–$10^5$ cm$^{-3}$ in the troposphere.$^1, 2$

1.2. Importance

Aerosols play major roles in environmental issues related to global and regional climate, the chemistry of the atmosphere, the hydrological cycle, and human health.$^3$–$^7$

Aerosols influence global and regional climate by direct or indirect effects. Aerosols can influence the earth’s energy budget directly by scattering and absorbing solar radiation, as well as outgoing terrestrial radiation.$^1$ Aerosols may modify cloud properties and the extent of precipitation by acting as cloud condensation nuclei (CCN) and ice nuclei (IN), indirectly affecting climate and the hydrological cycle.

People have been aware of adverse health effects due to the inhalation of aerosol particles for decades. When considering the health risks from aerosol particles, researchers usually focus on PM$_{2.5}$ (particulate matter < 2.5 μm), since these particles can be transported deep into the lungs when inhaled.$^1$ Numerous epidemiological studies have shown that fine aerosol particles are correlated with severe health effects, including enhanced mortality, cardiovascular, respiratory, and allergic diseases when inhaled and deposited in the human respiratory tract.$^2$–$^3, 8$–$^{11}$ Several studies have also suggested that heterogeneous oxidation and nitration reactions of aerosol particles can lead to the
formation of hazardous compounds which are more toxic than the precursor compounds.\cite{3, 12-15} Although the associations between the concentrations of particles and adverse health effects have been established, there is still little known about the possible mechanisms of damage, or which are the most toxic components in particles. It is thus important to understand both the chemical composition of aerosols as well as compositional changes due to atmospheric reactions.\cite{16, 17}

### 1.3. Composition of Aerosol Particles

Aerosol particles are complex multiphase systems consisting of a wide variety of organic and inorganic chemical compounds. The dominant inorganic species present in submicron aerosols are $\text{SO}_4^{2-}$, $\text{NO}_3^-$, and $\text{NH}_4^+$.\cite{1, 18} In contrast, the composition of organic species is much more complex and is currently poorly understood.\cite{19-21} Organic material can contribute 20–90% to the total submicron aerosol mass. However, depending on the location, time of day or year, specific meteorological conditions, and particle size, the relative abundance of different chemical components can vary significantly.\cite{22, 23} Figure 1.1 summarizes aerosol composition results from 30 field studies for urban and rural/remote areas around the world.\cite{19}
Figure 1.1: Pie charts showing the average mass concentration and chemical composition of submicron particles: organics (green), sulfate (red), nitrate (blue), ammonium (orange), and chloride (purple), taken from Zhang et al.\textsuperscript{19}

Depending on their origin, organic aerosols can be classified as primary or secondary. Primary organic aerosols are directly emitted into the atmosphere. Secondary organic aerosols are formed by chemical reaction and gas-to-particle conversion of their precursor volatile organic compounds in the atmosphere through oxidative aging.\textsuperscript{21, 24-30}

Many hundreds of organic compounds have been identified through chromatography and mass spectrometry techniques.\textsuperscript{19, 20, 31-36} However, even in the most comprehensive investigations, only about 10% of the organic particulate matter has been identified on a molecular level. Prominent organic substance classes identified in atmospheric particles and their main sources are summarized in Table 1.1.\textsuperscript{37}
Table 1.1: Prominent organic aerosol components, adapted from Pöschl.37

<table>
<thead>
<tr>
<th>Substance Classes</th>
<th>Upper limit of mass percentage</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>fatty acids and other alkanoic acids</td>
<td>10%</td>
<td>biomass, oxidation of VOCs&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>aliphatic dicarboxylic acids</td>
<td>10%</td>
<td>SOA&lt;sup&gt;b&lt;/sup&gt;/aging</td>
</tr>
<tr>
<td>aromatic (poly-) carboxylic acids</td>
<td>10%</td>
<td>SOA/aging, soil/dust</td>
</tr>
<tr>
<td>multifunctional aliphatic and aromatic compounds (OH, CO, COOH)</td>
<td>10%</td>
<td>SOA/aging, soil/dust</td>
</tr>
<tr>
<td>levoglucosan</td>
<td>10%</td>
<td>biomass burning</td>
</tr>
<tr>
<td>aliphatic hydrocarbons</td>
<td>1%</td>
<td>biomass, fossil-fuel combustion</td>
</tr>
<tr>
<td>aliphatic alcohols and carbonyls</td>
<td>1%</td>
<td>biomass, SOA/aging</td>
</tr>
<tr>
<td>proteins and other amino compounds</td>
<td>10%</td>
<td>biomass</td>
</tr>
<tr>
<td>secondary organic oligomers/polymers and humic-like substances</td>
<td>10%</td>
<td>SOA/aging, soil/dust</td>
</tr>
<tr>
<td>cellulose and other carbohydrates</td>
<td>1%</td>
<td>biomass</td>
</tr>
</tbody>
</table>

<sup>a</sup> Volatile organic compounds (VOCs)

<sup>b</sup> Secondary organic aerosol (SOA)

As each of these substance classes in Table 1.1 contains a variety of organic molecules, it is not feasible to study atmospheric reactions of all these compounds and include them all into modeling studies. It is therefore necessary to focus on organic functional groups and choose model compounds as typical representatives of certain classes of organic aerosol components including \(n\)-alkanoic acids, \(n\)-alkenoic acids, \(n\)-alkanes, alcohols, and \(n\)-alkanals. Sources of these compound classes are described in the following paragraphs.

Alkanes, alkanoic and alkenoic acids are ubiquitous components in organic aerosols. Alkanes and alkanoic acids are the major constituents of many organic aerosol
particles formed by both natural and anthropogenic processes. Sources include: road dust,\textsuperscript{38} meat cooking,\textsuperscript{36,39-41} vehicle exhaust,\textsuperscript{36,42,43} cigarette smoke,\textsuperscript{44} and residential and commercial heating.\textsuperscript{45,46} Alkenoic acids (e.g., oleic acid) are also found to be an important organic component of aerosols emitted from road dust\textsuperscript{38}, meat cooking\textsuperscript{39-41}, and biogenic sources\textsuperscript{47,48}. Alcohols are usually of biogenic origin,\textsuperscript{1} primarily from biomass burning\textsuperscript{31,48} or suspended biogenic detritus.\textsuperscript{1,47,49} Sources of \textit{n}-alkanals are both biological and anthropogenic in origin, ranging from biogenic emissions,\textsuperscript{50-54} meat-cooking operations,\textsuperscript{39,55,56} to automobiles.\textsuperscript{42}

1.4. Introduction to Heterogeneous Atmospheric Reactions

In the field of atmospheric chemistry, heterogeneous reactions are defined as reactions between gas-phase species and solid- or liquid-phase aerosol particles. For organic aerosols, this process is also known as oxidation or oxidative aging.\textsuperscript{57}

Heterogeneous reactions can play an important role in the atmosphere.\textsuperscript{1,24,58} They could modify physical properties such as the particle size and density, as well as the chemical composition of aerosol particles thereby affecting not only their optical properties (i.e., scattering and absorbing solar and terrestrial radiation) but also their hygroscopic properties (influencing cloud condensation nuclei (CCN) or ice nuclei (IN) properties).\textsuperscript{20,37,57} Heterogeneous chemistry can also change the gas-phase composition of the atmosphere. A prominent example is the formation of reactive halogen species that cause the depletion of stratospheric ozone over the Arctic and Antarctic regions.\textsuperscript{1} Heterogeneous reactions may also lead to the formation or degradation of hazardous aerosol components that affect human health.\textsuperscript{3,12-15,59} These reactions can be a loss pathway of organic compounds in the atmosphere, and under certain conditions, they can be an important sink for gas-phase species.\textsuperscript{24,37,57,60,61} Heterogeneous reactions 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.\textsuperscript{62}
Despite the fact that heterogeneous chemistry is of high importance, this field is still in its infancy and a better understanding of heterogeneous reactions is needed.\textsuperscript{3, 4, 63} While our understanding of gas-phase reactions (also called homogeneous reactions) is well established (with a range of different techniques available with good agreement among different laboratories), the study of heterogeneous reactions is a relatively new field of research and provides greater challenges.\textsuperscript{1} For example, the reaction kinetics for gas-phase radicals such as OH and NO\textsubscript{3} radicals with condensed-phase organic particles has only recently been investigated in laboratory studies.\textsuperscript{2, 29, 58, 64, 65}

1.5. Motivation for My Study

NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} are both abundant nighttime species and potential oxidants of aerosol particles. NO\textsubscript{3} is an important nighttime intermediate with concentration up to 430 ppt in polluted nighttime atmospheres.\textsuperscript{1} The concentration of N\textsubscript{2}O\textsubscript{5} at night was estimated as high as 10-15 ppb.\textsuperscript{66} Yet, current understanding of heterogeneous chemistry of NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} with organic particles is very limited.

In the area of NO\textsubscript{3} chemistry, recent work has shown that NO\textsubscript{3} can react with carbon-carbon double bonds quickly.\textsuperscript{64} But this was only studied with single component systems. The chemistry may be different in multicomponent systems which are better models for atmospheric particles. Thus, in this study, we investigated the reaction of NO\textsubscript{3} with binary mixtures containing an unsaturated organic (methyl oleate).

In addition to the NO\textsubscript{3} chemistry, the reactivity of NO\textsubscript{3} with several different organic classes has been studied recently.\textsuperscript{60, 64, 67} One class that could potentially react fast with NO\textsubscript{3} but has not studied is aldehydes. Here we studied the reactions of NO\textsubscript{3} with tridecanal and also NO\textsubscript{3} with binary mixtures comprising tridecanal.

In the area of N\textsubscript{2}O\textsubscript{5} chemistry, recent work has shown that the heterogeneous chemistry between glycerol and N\textsubscript{2}O\textsubscript{5} is rapid.\textsuperscript{64} But this was only based on one organic molecule. Here we expanded on this by investigating the reaction of N\textsubscript{2}O\textsubscript{5} with four organics that all contain hydroxyl groups.

The organic compounds chosen in this thesis are representatives of classes of
organic aerosol components in the atmosphere. Squalane was chosen as \( n \)-alkane, diethyl sebacate (DES) and dioctyl sebacate (DOS) were chosen as \( n \)-alkanoates, tridecanal was chosen as \( n \)-alkanal, poly ethylene glycol (PEG) and 1,2,6-trihydroxyhexane were chosen as alcohols, and methyl oleate was chosen as an representative of \( n \)-alkenoic acids.

1.6. Thesis Overview

This work investigates the kinetics of the heterogeneous reactions of NO\(_3\) and N\(_2\)O\(_5\) with pure organic substrates as well as with two-component mixtures (only for NO\(_3\)).

Chapter 1 briefly introduces the physical properties, chemical composition, and the importance of aerosol particles. In addition this chapter introduces heterogeneous reactions between gas-phase oxidants and aerosol particles and the importance of this topic. This leads to a discussion of the motivation of my study at the end of this chapter.

Chapter 2 provides some background information on heterogeneous reactions. This includes the definition of the reactive uptake coefficient (\( \gamma \)), and a discussion of interactions between gas-phase molecules and condensed phase substrates, and the “resistor model” and related equations used to express the overall uptake coefficient.

Chapter 3 presents the kinetics results of NO\(_3\) reactions with pure organic substrates and binary mixtures containing methyl oleate and other saturated compounds. This chapter demonstrates that the kinetics can vary by a factor of 5 depending on the type of saturated organics in the liquid mixtures. For liquid-solid mixtures, the kinetics decreases by a factor of 10 with 90 min NO\(_3\) exposure. Based on the kinetics results, the atmospheric lifetimes of unsaturated organics in liquid mixtures are estimated to be short (< 35 mins). For liquid-solid mixtures, the lifetime can be significantly longer (> 1-2 hours).

Chapter 4 provides reactive uptake coefficients for NO\(_3\) on solid tridecanal and binary mixtures containing tridecanal. The results show that the reaction between NO\(_3\) and aldehyde is fast. This chapter also presents the kinetics results for N\(_2\)O\(_5\) reaction with alcohols where uptake coefficients range from \( 8 \times 10^{-5} \) to \( 2 \times 10^{-2} \). These results lead to a
broad range of estimated lifetimes for pure alcohol particles with respect to N₂O₅ aging (i.e., from <1 hour to > 4 days). Finally, Chapter 5 provides a summary of research findings and suggestions for future work.
2 Background Information

2.1. The Reactive Uptake Coefficient (\(\gamma\))

The reactive uptake coefficient (\(\gamma\)) is defined as the fraction of collisions between the gas-phase species and the reactive surface that leads to irreversible uptake. This is a standard kinetics parameter used in chemical transport models to assess the atmospheric importance of the heterogeneous reactions.\(^{58}\) The reactive uptake coefficient also represents the net loss of a gas-phase species that reacts with the condensed phase. Hence, it describes the overall uptake without deconvoluting the individual steps involved.

2.2. Gas–Condensed Phase Interactions

The uptake of gas by a condensed phase involves complex interactions. Based on earlier studies\(^{1,68,69}\), this process can be described as: (1) gas phase diffusion, (2) adsorption and desorption at the surface, (3) reaction at the surface, (4) solvation of the gas-phase species and incorporation to the bulk liquid, (5) diffusion of gas in the bulk liquid, and (6) reaction in the bulk liquid. Some of these factors may not play a role in the uptake of a given species.

Figure 2.1 illustrates the steps for a flat surface.\(^{68}\) A gas-phase molecule diffuses through the air, collides with the surface, and either absorbs or scatters off the surface. An absorbed molecule can either desorb, react at the surface, or be taken up into the bulk liquid. If it diffuses through the bulk, it either reacts or evaporates again into the gas-phase. As discussed, the measured uptake coefficients in this thesis describe the net loss of gas-phase species for the overall process without consideration of the individual steps.
2.3. The Resistor Model

To properly describe the uptake with all the steps involved, the “resistor model” was developed. The different steps are treated as if they were components of an electrical circuit. Each physical or chemical process has a specific conductance $\Gamma$, and the resistance of each step is $\Gamma^{-1}$. Thus, each step in the gas–condensed phase interaction is formulated in terms of a resistance so that all the resistances can be combined in series or in parallel to obtain the overall rate ($\gamma$) of the heterogeneous process.68

Figure 2.2 provides a schematic of the resistor model for a gas-condensed phase interaction where $\Gamma_{\text{diff}}$ is the gas transport conductance, which is related to gas-phase diffusion, $S$ is the surface adsorption coefficient, $k_{\text{sol}}$ is the rate of solvation, $k_{\text{des}}$ is the rate of desorption, $\Gamma_{\text{sat}}$ represents the solubility of gas-phase species in the condensed-phase, $\Gamma_{\text{rxn}}$ is the conductance due to bulk reaction, and $\Gamma_{\text{surf}}$ is the conductance due to surface reaction.68
Figure 2.2: Schematic of the resistance model treating individual chemical and physical processes involved in the uptake of a gas-phase species into a liquid as resistances in an electrical circuit, adapted from Davidovits et al.\textsuperscript{68}

By using the resistor model, the reactive uptake coefficient can be expressed by the following equations:

(1) With all the steps in Figure 2.2 involved.

\[
\frac{1}{\gamma} = \frac{1}{\Gamma_{\text{diff}}} + \frac{1}{S} + \frac{1}{\frac{1}{\Gamma_{\text{rxn}}} + \frac{1}{\Gamma_{\text{sat}}} + \frac{1}{\frac{k_{\text{sol}}}{k_{\text{des}}} S}} + \frac{1}{\Gamma_{\text{surf}}}
\]

(2) If the bulk reaction dominates (the conductance of surface reaction can be ignored):

\[
\frac{1}{\gamma} = \frac{1}{S} + \frac{1}{\frac{1}{\Gamma_{\text{rxn}}} + \frac{1}{\Gamma_{\text{sat}}} + \frac{1}{\frac{k_{\text{sol}}}{k_{\text{des}}} S}} + \frac{1}{\Gamma_{\text{surf}}}
\]
Jayne et al. presented an equation relating the mass accommodation coefficient ($\alpha$) to the adsorption coefficient ($S$).\(^{70}\)

\[ \frac{1}{\gamma} = \frac{1}{S} + \frac{1}{S \frac{k_{sol}}{k_{des}}} + \frac{1}{\Gamma_{rxn} + \Gamma_{sat}}. \]

Thus, E 2.3 can be simplified as:

\[ \frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{\Gamma_{rxn} + \Gamma_{sat}} \]

The conductance for saturation ($\Gamma_{sat}$) reflects the increasing rate of evaporation of dissolved gas-phase species back into the gas phase when the solubility limit is approached. In our experiments, as no excess NO\(_3\) is released after the steady state is reached, the conductance for saturation ($\Gamma_{sat}$) equals zero. As a result the reactive uptake can be approximated as the following:

\[ \frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{\Gamma_{rxn}} \]

where the conductance for the bulk reaction, $\Gamma_{rxn} = \frac{4RTH}{c_{avg}} \sqrt{Dk_{2}M}$. \(H\) is the Henry’s law solubility constant of gas-phase species in the condensed phase liquid, \(R\) is the gas constant, \(T\) is the temperature, \(D\) is the diffusion coefficient for gas-phase species in the condensed phase, \(k_{2}\) is the bulk second-order rate constant for the bulk reaction, \(c_{avg}\) is the mean molecular velocity of gas-phase species, and \(M\) is the molarity of the condensed phase liquid.

(3) If reaction occurs at the surface only:

\[ \frac{1}{\gamma} = \frac{1}{S} + \frac{1}{\Gamma_{surf}} \]
where the conductance for the surface reaction, $\Gamma_{surf} = \frac{4RT H^S K^S k_{2v}^S M}{c_{avg}}$. In this equation, $H^S$ is surface analog to a Henry’s law equilibrium for bulk condensed phase, $K^S$ is equilibrium constant linking the surface concentration to the bulk concentration of the condensed phase liquid, and $k_{2v}^S$ is the second-order rate constant for the reaction at the surface.

E 2.6 and E 2.7 derived above are used to analyze our results in Chapters 3 and 4.
3 The Effect of the Matrix on the NO₃ Heterogeneous Kinetics with Unsaturated Organics

3.1. Introduction

Organic material contributes about 20-90% to the total fine aerosol mass in the troposphere.¹⁹, ²¹ This organic material can be in the form of pure organic particles or alternatively the organic can be internally mixed with inorganic material.⁷¹, ⁷² Organic and mixed organic-inorganic particles can be solids, liquids, liquid-liquid mixtures, liquid-solid mixtures or glasses.⁷³-⁸² While in the atmosphere these organic and mixed organic-inorganic particles can undergo heterogeneous reactions with reactive gas-phase species such as OH,⁵⁸, ⁸³-⁸⁵, O₃,²⁹, ⁸⁶-⁸⁹, NO₃,²⁸, ⁶⁰, ⁶⁴, ⁹⁰-⁹⁴ and Cl⁶¹, ⁹⁵, ⁹⁶.

Despite the potential importance of organic heterogeneous chemistry in the atmosphere and the fact that organic particles in the atmosphere are complex, there have been relatively few heterogeneous chemistry studies using multicomponent or multiphase organic mixtures. Recent studies using multicomponent and multiphase organics have mainly involved O₃, OH and Cl chemistry. See for example references⁷⁵, ⁸⁶, ⁸⁸, ⁹¹, ⁹⁵-¹¹⁵.

Recently we studied the reactive uptake coefficient of NO₃ on single-component organics and concluded that the NO₃-alkene reaction could potentially be an important loss process of particle-phase unsaturated organic compounds in the atmosphere and in laboratory secondary organic aerosol studies.⁶⁴ However, these conclusions were based on measurements with single-component substrates. The NO₃ kinetics may be different in multicomponent and multiphase mixtures based on past studies using multicomponent and multiphase mixtures with O₃, OH and Cl. See for example references⁵⁸, ⁷⁵, ⁸⁷, ⁸⁸, ⁹¹, ⁹⁶-¹⁰⁰, ¹⁰², ¹⁰³, ¹⁰⁸, ¹¹⁰, ¹¹³, ¹¹⁴, ¹¹⁶.

In the following we investigate NO₃ reactive uptake on multicomponent and multiphase mixtures containing an unsaturated organic. For the unsaturated organic we used methyl oleate (see Figure 3.1). Based on previous work we expected that the reaction between NO₃ and the carbon-carbon double bond is efficient and the ester functional group does not play a significant role in the chemistry or kinetics.⁶⁴ Other
molecules used in this study were diethyl sebacate (DES), dioctyl sebacate (DOS), and squalane. These molecules cover a range of viscosities, molecular weights and functional groups (See Figure 3.1 and Table 3.1). Also these molecules have low vapor pressures (which is prerequisite for the flow tube studies). Here we refer to these saturated organics as matrix molecules.

At a temperature of 278 K we studied the following binary mixtures: methyl oleate-DES, methyl oleate-DOS and methyl oleate-squalane. At this temperature the mixtures were all liquid. This allowed us to probe multicomponent liquid mixtures and assess the effect of the matrix molecules on the NO$_3$ uptake kinetics. At 268 K we studied binary mixtures of methyl oleate-DES. At this temperature the binary system was a solid-liquid mixture. This allowed us to probe the effect of particle phase on the NO$_3$ chemistry. In all experiments the concentration of methyl oleate in the binary mixtures were always kept less than 4 wt% methyl oleate. At these concentrations physical properties of the binary mixtures, such as solubility and molecular diffusion, will be controlled mainly by the matrix molecules.

Below we present the reactive uptake coefficient measurements for these multicomponent and multiphase mixtures. The results are analyzed using the resistor model, and the results from this analysis are then used to assess the effect of the matrix molecules on the NO$_3$ uptake kinetics and the lifetime of unsaturated organics in the atmosphere.
Table 3.1: Properties of the organic compounds used in this study

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Formula</th>
<th>Molecular weight (g/mole)</th>
<th>Viscosity at 293-298 K (mPa·s)</th>
<th>Diffusion Coefficient(^a) at 293K (cm(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl oleate</td>
<td>C(<em>{19})H(</em>{36})O(_2)</td>
<td>296.49</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>DES</td>
<td>C(<em>{14})H(</em>{26})O(_4)</td>
<td>258.36</td>
<td>5.88(^{117})</td>
<td>1.8×10(^{-6})</td>
</tr>
<tr>
<td>DOS</td>
<td>C(<em>{26})H(</em>{50})O(_4)</td>
<td>426.67</td>
<td>25(^b)</td>
<td>4.3×10(^{-7})</td>
</tr>
<tr>
<td>squalane</td>
<td>C(<em>{30})H(</em>{62})</td>
<td>422.81</td>
<td>36.0(^{118})</td>
<td>3.0×10(^{-7})</td>
</tr>
</tbody>
</table>

\(^a\) The diffusion coefficient is calculated by the Stokes-Einstein equation\(^{64}\) and by assuming the radius of the diffusing species (NO\(_3\)) was the same as O\(_3\) as done in a recent paper.\(^{119}\)

\(^b\) Taken from www.kicgroup.com/dos.htm
3.2. Experimental

3.2.1. Experimental Setup and Procedure

Experiments were conducted in a cylindrical, rotating-wall flow tube reactor coupled to a chemical ionization mass spectrometer (CIMS). The experimental setup was provided in Figure 3.2. A rotating Pyrex tube (~12 cm length, 1.77 cm inner diameter) fit snugly inside the flow tube reactor. The inside wall of the glass tube provided a surface for a thin coating of the studied organic material. NO₃ entered the flow tube through a movable injector. By varying the distance between the injector tip and the exit of the flow tube, loss of NO₃ can be determined as a function of reaction distance and thus reaction time.

NO₃ radicals were obtained by thermal conversion of gaseous N₂O₅ to NO₃ and NO₂ at 430 K in a Teflon coated glass oven before entering the movable injector. N₂O₅ was generated by reacting NO₂ with an excess amount of O₃ in a flow system as described by Schott and Davidson¹²⁰ and Cosman et al.¹²¹ N₂O₅ was trapped and stored as solid white crystals at 197 K.

After thermal conversion of N₂O₅ to NO₃ and NO₂, the recombination of NO₃ and NO₂ was negligible due to the short residence time of the gases in the flow tube reactor (typically 20–100 ms), NO₃ was detected as NO₃⁻ in the mass spectrometer after chemical ionization by I⁻ which was generated by passing a trace amount of CH₃I in N₂ through a ²¹⁰Po source (model Po-2031, NRD).

Total pressures in the flow cell during experiments were typically 2.6–3.2 Torr whereas flow velocities ranged from 380–600 cm s⁻¹. The carrier gas through the cell was a mixture of O₂ (~10–15%) in He. NO₃ concentrations for all experiments were estimated as (3.5–16)×10¹⁰ molecules cm⁻³ 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.¹²² Quantitative conversion of N₂O₅ to NO₃ and NO₂ in the oven was confirmed by adding high levels of NO to the exit of the flow tube.
This conversion reaction with NO also served as a convenient way to quantify the background signal in the NO$_3$ experiments. The background signal was typically less than 10% of the total signal. The uncertainty of the NO$_3$ concentration, based on the uncertainty of the rate constant for the gas-phase N$_2$O$_5$ + I$^-$ reaction, is 40%. \textsuperscript{123}

\textbf{Figure 3.2:} Experimental setup for NO$_3$ and N$_2$O$_5$ experiments — the rotating wall flow tube reactor coupled to a chemical ionization mass spectrometer (CIMS).

From the collected CIMS traces, plots were generated for the natural logarithm of the depletion of the relative NO$_3$ signal as a function of reaction time (Figure 3.2). The reaction time was calculated based on the distance from the injector tip to the exit of the
flow tube and the flow velocity of NO₃ in the reaction cell. The slopes of the linear fits were used to determine the observed first-order loss rate coefficients, $k_{\text{obs}}$. Corrections for both radial and axial diffusion were applied to all $k_{\text{obs}}$ values using the formulations described by Brown¹²⁴ and Howard¹²⁵. Uptake coefficients ($\gamma$) were calculated from the corrected rate constants, $k_{\text{corr}}$, using a standard procedure.⁷⁵ Diffusion coefficients of NO₃ used in these calculations were taken from Rudich et al.¹²⁶

![Figure 3.3: Plot of the natural logarithm of the NO₃ signal vs. reaction time from several experiments. The substrates used in these studies were liquid DES and two liquid binary mixtures of methyl oleate and DES (0.57 and 1.72 wt% methyl oleate).](image)

The two main sources of uncertainty for the uptake coefficient measurements were the gas phase NO₃ diffusion coefficient and the measurement of $k_{\text{obs}}$. We calculated the error from gas phase diffusion by assuming a 20% uncertainty of the NO₃ diffusion coefficient. For the uncertainty of $k_{\text{obs}}$, we used the standard deviation (1σ) of the measurements. Reported errors include both the uncertainty from the diffusion coefficient and uncertainty from measuring $k_{\text{obs}}$. 
For reactive uptake studies on liquids, approximately 0.5 to 0.8 ml of the liquid was added to the inner wall of a rotating glass cylinder. A rotation rate of ~10 rotations min–1 was used for all experiments to ensure an even coating of the liquid on the inside of the glass tube.

For reactive uptake studies on solid-liquid mixtures, a smooth solid-liquid film was prepared following the procedure outlined by Knopf et al. First a liquid mixture of methyl oleate in DES (1.4 wt % methyl oleate) was prepared. This liquid mixture was added to a glass tube at room temperature and rotated. Next, the glass tube was rapidly immersed into liquid N₂. Subsequently, the tube was taken out of the liquid N₂ and located inside the flow tube reactor at (268±1) K.

3.2.2. Measurements of the Temperature-Composition Phase Diagram for Mixtures of Methyl Oleate in DES

The temperature-composition phase diagram for methyl oleate-DES mixtures is not known. We determined this phase diagram by means of differential scanning calorimetry (DSC). The phase diagram was necessary to determine properties of the solid phase (e.g. pure solid DES or a solid solution containing methyl oleate and DES) that formed in the experiments mentioned above as well as determine mass partitioning between solid and liquid phases.

Determination of the phase diagram consisted of the following steps: 40 μL of liquid mixture (methyl oleate and DES) were added to a sample pan. The temperature of the sample was decreased to -50°C, and then increased to 30°C at a rate of 5 °C/min. The phase diagram was constructed from the melting peaks in the thermogram.

3.2.3. Chemicals

Diethyl sebacate (98%) and squalane (99%) were obtained from Sigma-Aldrich; Methyl oleate (≥ 99%) and dioctyl sebacate (≥ 97%) were purchased from Fluka; NO₂ was purchased from Matheson. N₂ (99.999%), O₂ (99.993%), and He (99.999%) were purchased from Praxiar. O₃ was produced by photolysis of O₂.
3.3. Results and Discussion

3.3.1. Reactive Uptake Coefficients of NO\textsubscript{3} on Single Component Organics

The resistor model is used to analyze the reactive uptake data for binary mixtures. Ideally, for this analysis the NO\textsubscript{3} reactive uptake coefficient on the pure matrix molecules are available. Table 3.2 provides the uptake coefficients for NO\textsubscript{3} on the pure matrix molecules, as well as the uptake on pure methyl oleate for comparison.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T (K)</th>
<th>Phase</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DES</td>
<td>278</td>
<td>Liquid</td>
<td>$(4.4 \pm 0.4) \times 10^{-3}$</td>
</tr>
<tr>
<td>DES</td>
<td>272</td>
<td>Solid</td>
<td>$(3.6 \pm 0.5) \times 10^{-4}\textsuperscript{a}$</td>
</tr>
<tr>
<td>DOS</td>
<td>278</td>
<td>Liquid</td>
<td>$(3.9 \pm 0.3) \times 10^{-3}$</td>
</tr>
<tr>
<td>squalane</td>
<td>278</td>
<td>Liquid</td>
<td>$(5.2 \pm 0.4) \times 10^{-3}$</td>
</tr>
<tr>
<td>methyl oleate</td>
<td>278</td>
<td>Liquid</td>
<td>$(1.4 \pm 8.6/-0.5) \times 10^{-1}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} This uptake coefficient was obtained from our previous work.\textsuperscript{64}

The uptake result for methyl oleate is in good agreement with measurements of other unsaturated organics (oleic acid, linoleic acid and conjugated linoleic acid).\textsuperscript{64} Also, the uptake coefficient of NO\textsubscript{3} on methyl oleate is about two orders of magnitude higher than those of NO\textsubscript{3} on saturated organics (DES, DOS and squalane). This trend is roughly consistent with the trend observed in the gas phase.\textsuperscript{128} The uptake coefficient of NO\textsubscript{3} with solid DES is about 90\% lower than the corresponding liquid-phase data.
3.3.2. Reactive Uptake Coefficients of NO$_3$ on Binary Liquid Mixtures Containing Methyl Oleate

Figure 3.3 shows the measured uptake coefficients of NO$_3$ on different binary mixtures as a function of the methyl oleate concentration. For all matrices studied the addition of small amounts of methyl oleate (less than 4 wt %) significantly increases the reactive uptake coefficient. Also, the magnitude of increase depends of the type of matrix. For example at approximately 2.3 wt % methyl oleate the reactive uptake coefficient in DES increased by a factor of 20 compared to the pure case, but in squalane the reactive uptake coefficient only increased by a factor of 4.

![Graph showing the measured uptake coefficients of NO$_3$ on binary liquid mixtures containing methyl oleate.](image)

Figure 3.4: Measured uptake coefficients of NO$_3$ on binary liquid mixtures containing methyl oleate. Some of the error bars for methyl oleate in DES exceed maximum y-values shown in this figure. Typically, when the $\gamma$ value is greater than 0.05 such as the last three data points for the methyl oleate-DES mixtures, the gas-phase diffusion of NO$_3$ to the reactive surface greatly influences the measured $\gamma$ values. In this case, a small uncertainty in the diffusion coefficient will result in a large uncertainty in the measured $\gamma$ value. All experiments were carried out at (278
To check whether the uptake is reversible or irreversible, at the end of every experiment we moved the injector to a position where the coated organic mixture was no longer exposed to the NO$_3$ flow. The absence of any release of NO$_3$ indicated that the uptake was irreversible.

3.3.3. Analysis of the Reactive Uptake Coefficient Data Using the Resistor Model

To analyze the liquid uptake results presented in Figure 3.3, we used the resistor model for gas-substrate interactions. If the reaction occurs in the bulk and the reactive uptake coefficient is not limited by the mass accommodation coefficient (i.e., $\alpha >> \gamma$, where $\alpha$ is the mass accommodation coefficient) then the following equation applies for our binary liquid mixtures (see Chapter 2.3 for the basic equations and further details in the Appendix):

$$E 3.1 \quad \gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2 = \frac{(4H_{\text{matrix}}RT)^2 D_{\text{matrix}} k_{\text{oleate}}}{c_{\text{NO}_3}^2} M_{\text{oleate}}$$

where $\gamma_{\text{mixture}}$ is the reactive uptake coefficient of NO$_3$ in the two component mixture, $\gamma_{\text{matrix}}$ is the reactive uptake coefficient of NO$_3$ with the pure matrix molecules, $H_{\text{matrix}}$ is the Henry’s law solubility constant of NO$_3$ in the matrix, $R$ is the gas constant, $T$ is the temperature, $D_{\text{matrix}}$ is the diffusion coefficient for NO$_3$ in the matrix, $k_{\text{oleate}}$ is the bulk second-order rate constant for the NO$_3$ reaction with methyl oleate, $c_{\text{NO}_3}$ is the mean molecular velocity of NO$_3$, and $M_{\text{oleate}}$ is the molarity of the methyl oleate in each matrix. According to $E 3.1$, a plot of $(\gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2)$ vs. $M_{\text{oleate}}$ is expected to yield a straight line.

In contrast to $E 3.1$, if the reaction occurs on the surface and assuming the reactive uptake coefficient is not limited by the adsorption coefficient, the following equation applies for our binary liquid mixtures (see Chapter 2.3 for the basics equations and the Appendix for further details):
\[ \gamma_{\text{mixture}} - \gamma_{\text{matrix}} = \frac{4H_{\text{matrix}}^S RTK_{\text{matrix}}^S k_{\text{oleate}}^S}{c_{\text{NO}_3}} M_{\text{oleate}} \]

where \( \gamma_{\text{mixture}} \) is the reactive uptake coefficient of NO\(_3\) with the binary mixture, \( \gamma_{\text{matrix}} \) is the reactive uptake coefficient of NO\(_3\) with the corresponding pure matrix, \( H_{\text{matrix}}^S \) is surface analogous to a Henry’s law equilibrium for bulk condensed phase, \( K_{\text{matrix}}^S \) is an equilibrium constant linking the surface concentration to the bulk concentration of the organic liquid, \( k_{\text{oleate}}^S \) is the second-order rate constant for the NO\(_3\) reaction with methyl oleate at the surface, and \( M_{\text{oleate}} \) is the molarity of methyl oleate in each matrix. If the reaction occurs at the surface and the assumptions outlined above are valid, then a plot of \((\gamma_{\text{mixture}} - \gamma_{\text{matrix}})\) vs. \( M_{\text{oleate}} \) is expected to yield a straight line.

In Figure 3.4 panels a-c, we have plotted \((\gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2)\) vs. \( M_{\text{oleate}} \) and panels d-f, we have plotted \((\gamma_{\text{mixture}} - \gamma_{\text{matrix}})\) vs. \( M_{\text{oleate}} \). Figure 3.4 shows that the data can be fit reasonably well by assuming either a bulk reaction or a surface reaction. To evaluate the goodness-of-fit for the two different models (bulk and surface), we calculated \( \chi^2 \) values. The results from these calculations are included in Figure 3.4. Based on the \( \chi^2 \) values, kinetics for DOS and squalane mixtures are explained well by both the bulk and surface model. For DES, the kinetic data fit better to the surface model than the bulk model, although even the bulk model does a reasonable job of describing the trend in the reactive uptake data.
Figure 3.5: Plot \( (\gamma_{\text{mixture}} - \gamma_{\text{matrix}})^2 \) (panel a, b, c) and \( (\gamma_{\text{mixture}} - \gamma_{\text{matrix}})^2 \) (panel d, e, f) as a function of \( M_{\text{oleate}} \). Panel a and d correspond to the reaction of NO\(_3\) with a methyl oleate-DES mixture, panel b and e correspond to the reaction of NO\(_3\) with methyl oleate-DOS mixtures, panel c and f correspond to the reaction of NO\(_3\) with methyl oleate-squalane mixtures.

Table 3.3 shows values of \( H_{\text{matrix}} \sqrt{D_{\text{matrix}} k_{\text{oleate}}} \) and \( H_{\text{matrix}}^S K_{\text{matrix}}^S k_{\text{oleate}}^S \) determined from the slopes of the lines shown in Figure 3.4. If the reaction occurs in the bulk, then the \( H_{\text{matrix}} \sqrt{D_{\text{matrix}} k_{\text{oleate}}} \) values vary by a factor of 2.7. If the reaction occurs on the surface, then the \( H_{\text{matrix}}^S K_{\text{matrix}}^S k_{\text{oleate}}^S \) values vary by a factor of 3.6. This shows that the matrix has an effect on the kinetics as expected. It is also interesting to compare the trends observed for the different matrices. For example the trend in \( H_{\text{matrix}} \sqrt{D_{\text{matrix}} k_{\text{oleate}}} \) is DES > DOS > squalane. This trend is the same as the trend in the diffusion coefficients \( D_{\text{matrix}} \) of the matrices (see Table 3.1).
Table 3.3:  $H_{\text{matrix}} \sqrt{D_{\text{matrix}} k_{\text{oleate}}}$ and $H^S_{\text{matrix}} K^S_{\text{matrix}} k^S_{\text{oleate}}$ values determined from the slopes of the lines in Figure 3.4. The reported uncertainties are based on the standard deviation (1σ) of the slopes in Figure 3.4.

<table>
<thead>
<tr>
<th>Matrix molecule</th>
<th>$H_{\text{matrix}} \sqrt{D_{\text{matrix}} k_{\text{oleate}}}$ (cm M$^{1/2}$ atm$^{-1}$ s$^{-1}$)</th>
<th>$H^S_{\text{matrix}} K^S_{\text{matrix}} k^S_{\text{oleate}}$ (L cm$^{-2}$ atm$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DES</td>
<td>69.4 ± 5.8</td>
<td>281.3 ± 11.8</td>
</tr>
<tr>
<td>DOS</td>
<td>35.4 ± 2.4</td>
<td>120.9 ± 4.2</td>
</tr>
<tr>
<td>squalane</td>
<td>26.1 ± 1.5</td>
<td>78.0 ± 2.7</td>
</tr>
</tbody>
</table>

3.3.4. Temperature-Composition Phase Diagram for Methyl Oleate-DES Mixtures

Shown in Figure 3.5 are results from the differential calorimetry measurements. According to the phase diagram, methyl oleate and DES are miscible in the liquid state but immiscible in the solid state. The eutectic temperature for the binary system was determined to be (250.7 ± 0.5) K.
Figure 3.6: Temperature-composition phase diagram for the methyl oleate-DES system. S and L indicate solid and liquid phases, respectively. MO represents methyl oleate. The symbols ■ and ▼ represent the melting temperatures of DES and methyl oleate, respectively, in the binary mixtures. The symbol ● represents the measured eutectic temperature of the mixture. Each point represents the average of two runs. The symbol ▲ represents the conditions at which the uptake kinetics was investigated. The line and curves were added to guide the eye.

3.3.5. Reactive Uptake Coefficient Measurements of NO₃ on Solid-Liquid Mixtures Containing Methyl Oleate and DES

The solid triangle in Figure 3.5 shows the temperature and composition at which we studied the reactive uptake coefficient of partially solid mixtures of methyl oleate and DES. According to the phase diagram, the mixture consists of solid DES in equilibrium with a binary liquid mixture of approximately 45 wt % methyl oleate in DES.

Contrary to measurements with liquids, the measured reactive uptake coefficients for these mixtures decrease with time. This is illustrated in Figure 3.6. After approximately 90 minutes the reactive uptake coefficient on the solid-liquid mixture decreased by a factor of 10. In contrast the reactive uptake coefficient of NO₃ on a liquid
methyl oleate-DES mixture with the same weight percent methyl oleate did not decrease with time as expected. Figure 3.6 illustrates that the phase of the mixture can significantly influence the kinetics, consistent with previous measurements using O₃, Cl and OH as the oxidants. See for example references 58, 75, 91, 96-100, 103, 108, 110, 116

![Figure 3.6](image-url)

**Figure 3.6:** Illustrates that the phase of the mixture can significantly influence the kinetics, consistent with previous measurements using O₃, Cl and OH as the oxidants. See for example references 58, 75, 91, 96-100, 103, 108, 110, 116.

![Figure 3.7](image-url)

**Figure 3.7:** Measured uptake coefficient ($\gamma$) of NO$_3$ on mixtures of methyl oleate with DES (composition = 1.37 wt % methyl oleate). Experiments were carried out by continuously exposing the surface to NO$_3$, and periodically measuring the NO$_3$ uptake coefficients. The open symbols represent experiments carried out at 278K and correspond to a liquid, whereas the solid symbols represent experiments carried out at 268K and correspond to a solid-liquid mixture.

In our studies the liquid – solid mixture is likely to have a surface that is partially solid DES and partially a liquid mixture of methyl oleate and DES. As the carbon-carbon double bonds in the exposed liquid regions are oxidized, the uptake is expected to decrease, consistent with observations.
3.4. Atmospheric Implications

3.4.1. Lifetime of Unsaturated Organics in Liquid Organic Particles

The atmospheric lifetime (τ) which can also be referred to as “lifetime”, is defined as the time it takes for the concentration of the reactant to drop to 1/e of its initial value (e is the base of natural logarithms, 2.718). Next we use the kinetic parameters for the liquids, to estimate the lifetime of condensed-phase unsaturated organics in the atmosphere. If the reaction occurs in the bulk, the following equation can be used together with parameters shown in Table 3.3 to estimate the atmospheric lifetime:\(^\text{69, 129, 130}\)

\[
E_{\text{3.3}} \sqrt{[\text{Unsaturated Organic}]}_t = \sqrt{[\text{Unsaturated Organic}]}_0 - \frac{3P_{\text{NO}_3} H_{\text{matrix}} D_{\text{matrix}} K_{\text{oleate}}}{2r_{\text{particle}}} t
\]

where \(P_{\text{NO}_3}\) is the NO\(_3\) partial pressure in the atmosphere, \(r_{\text{particle}}\) is the radius of the particle in the atmosphere, \([\text{Unsaturated Organic} ]_0\) is the initial concentration of the unsaturated organic in the particle and \([\text{Unsaturated Organic} ]_t\) is the concentration of an unsaturated organic after reaction time \(t\).

If the reaction occurs at the surface than the following equation together with parameters in Table 3.3 can be used to estimate the lifetime of an unsaturated organic in the atmosphere:\(^\text{69}\)

\[
E_{\text{3.4}} \ln \frac{[\text{Unsaturated Organic} ]_t}{[\text{Unsaturated Organic} ]_0} = -\frac{3P_{\text{NO}_3} H_{\text{matrix}}^S K_{\text{matrix}}^S K_{\text{oleate}}^S}{r_{\text{particle}}} t
\]

Shown in Table 3.4 are the calculated lifetimes of unsaturated organics using E 3.3 and E 3.4, the parameters listed in Table 3.3, a particle radius of 100 nm, and a NO\(_3\) concentration of 25 ppt NO\(_3\) (24 hours average). The NO\(_3\) concentration corresponds to roughly moderately polluted levels.\(^\text{131}\)
Table 3.4: Estimated atmospheric lifetimes of unsaturated organics, $\tau_{\text{unsaturated}}$, using parameters determined from studies with methyl oleate in different matrices (DES, DOS and squalane).

<table>
<thead>
<tr>
<th>System used for determining kinetic parameters</th>
<th>$\tau_{\text{unsaturated}}$ (min)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Assuming Bulk Reaction</td>
</tr>
<tr>
<td></td>
<td>Assuming Surface Reaction</td>
</tr>
<tr>
<td>Liquid mixture of methyl oleate in DES</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
</tr>
<tr>
<td>Liquid mixture of Methyl oleate in DOS</td>
<td>25.7</td>
</tr>
<tr>
<td></td>
<td>18.4</td>
</tr>
<tr>
<td>Liquid mixture of methyl oleate in squalane</td>
<td>34.8</td>
</tr>
<tr>
<td></td>
<td>28.5</td>
</tr>
<tr>
<td>Solid-liquid mixture of methyl oleate in DES</td>
<td>&gt; 117.2</td>
</tr>
<tr>
<td></td>
<td>&gt; 64.2</td>
</tr>
</tbody>
</table>

$^a$ When calculating the atmospheric lifetime it was assume that the mole fraction of the unsaturated organic in the particle was 0.1 and the particle radius was 100 nm.

Several conclusions can be drawn from Table 3.4. First, comparing the calculations assuming bulk with the calculations assuming surface, the lifetimes only differ by a factor of 1.5. Second, the lifetimes differ by only factor of 3 when comparing different liquid matrices. Third, regardless of the liquid matrix, or the assumption of surface vs. bulk, the lifetimes are short (all less than 35 min) for liquids. Hence we can conclude that the lifetime of unsaturated organics (similar to methyl oleate) are likely short in the atmosphere if the particle matrix is in a liquid state and NO$_3$ concentrations are approximately 25 ppt, and the diffusion coefficient of the unsaturated organics in the matrix is greater than $10^{-10}$ to $10^{-15}$ cm$^2$ s$^{-1}$. At smaller diffusion coefficients the reactive uptake can be limited by the diffusion of the unsaturated compounds in the particle. As a result, different equations other than E 3.3 and E 3.4 would be used to calculate the lifetime of the particle. 69, 119, 132
3.4.2. Lifetime of Unsaturated Organics in Semi-Solid Organic Matrices

Following a similar approach to Chapter 3.4.1, we can estimate a lifetime of an unsaturated organic in a semi-solid particle in the atmosphere. In this case lifetimes were calculated using the reactive uptake coefficients measured at an NO$_3$ exposure of 90 min. These lifetimes should be considered lower limits, since the reactive uptake coefficient is still decreasing at an exposure of 90 minutes. Results from these calculations are included in Table 3.4, last row. Table 3.4 illustrates that the lifetime of unsaturated organics can be significantly longer in semi-solid particles.
4 Potentially Important Nighttime Heterogeneous Chemistry: NO$_3$ with Aldehydes and N$_2$O$_5$ with Alcohols

4.1. Introduction

Recently we investigated the reactive uptake of N$_2$O$_5$ on a range of organic substrates including oleic acid, DES, glycerol, and linoleic acid.$^{64}$ That study showed that the reactive uptake coefficient of N$_2$O$_5$ on liquid glycerol is relatively large with a value of (3.2–8.5)$\times10^{-4}$, suggesting that N$_2$O$_5$ heterogeneous reactions with alcohols may be atmospherically relevant. However, the N$_2$O$_5$–alcohol uptake results from Gross et al.$^{64}$ only examined one alcohol compound, glycerol, thus additional studies with other alcohols are also needed to determine the generality of the results. We have also recently explored the reactive uptake of NO$_3$ on a range of organic substrates with diverse functionalities.$^{64, 67, 90, 92, 93}$ One reaction class that has not been studied, however, are those reactions of NO$_3$ with condensed phase aldehydes. This reaction is known to be fast in the gas-phase and so the expectation is that it will also be fast in the condensed phase.

We have determined in this investigation the kinetics for N$_2$O$_5$ reactions with alcohols and NO$_3$ reactions with aldehydes. This information is then used to assess the lifetime of alcohols and aldehydes in the condensed phase in the atmosphere. For the N$_2$O$_5$ reactions we studied the uptake on five different liquid alcohols at (275±1) K. For the NO$_3$ reaction we studied the kinetics with the C$_{13}$ aldehyde tridecanal. The uptake of NO$_3$ on the solid C$_{13}$ aldehyde was determined at (263±1) K. For the pure aldehyde we were limited to this temperature since the vapor pressure of the aldehyde was high. To explore the reactions of NO$_3$ with aldehydes in the liquid state we studied several binary mixtures of tridecanal with DES, DOS, and squalane. By using binary mixtures where the concentration of the aldehyde is less than 6% w/w, the overall partial pressure of the aldehyde in the gas phase was reduced (which is a practical requirement for these flow tube studies). The study of binary mixtures also has the added advantage in that we could assess the importance of the matrix molecules on the NO$_3$–aldehyde kinetics.
4.2. Experimental

4.2.1. Experimental Setup and Procedure

The setup and procedure for the NO$_3$ uptake experiments were discussed in detail in Chapter 3.2.1. The uptake experiments for N$_2$O$_5$ were conducted in the same manner as NO$_3$. The N$_2$O$_5$ concentration inside the flow tube was estimated to be $(3.6-8.5)\times10^{11}$ molecules cm$^{-3}$ based on the rate constant for the gas-phase N$_2$O$_5$ + I$^-$ reaction. Similar to that of NO$_3$, a natural logarithm of the depletion of the N$_2$O$_5$ signal as a function of reaction time was used to calculate $k_{obs}$. Corrections for both radial and axial diffusion were applied to all $k_{obs}$ values using the formulations described by Brown$^{124}$ and Howard$^{125}$. Uptake coefficients ($\gamma$) were calculated from the corrected rate constants, $k_{corr}$, using a standard procedure.$^{75}$ Diffusion coefficients used within these calculations were taken from Knopf et al.$^{133}$

4.2.2. Chemicals

Tridecanal, ($\geq95\%$), squalane (99%), diethyl sebacate (98%), bis(2-ethylhexyl) sebacate (or dioctyl sebacate) ($\geq97.0\%$), poly(ethylene glycol) (PEG-300 and PEG-400), (+)-diethyl L-tartrate (<99%), and 1,2,6-trihydroxyhexane (96%) were obtained from Sigma-Aldrich. All chemicals were used as delivered. NO$_2$ (99.5%) was acquired from Matheson while N$_2$ (99.999%), O$_2$ (99.993%), and He (99.999%) gases were procured from Praxair. Figure 4.1 provides molecular structures for the organic compounds studied.
4.3. Results and Discussion

4.3.1. Kinetics of the NO$_3$ Reaction with Solid Tridecanal and Liquid Binary Mixtures of Tridecanal with Matrix Molecules

For the uptake of NO$_3$ on pure solid tridecanal at (263±1) K, seven reactive uptake coefficients were measured. The mean $\gamma$ value was determined as $(1.6 \pm 0.8) \times 10^{-2}$. Table 4.1 provides a comparison of our measured uptake coefficients with those uptake coefficients of NO$_3$ measured on other single component solid surfaces. Table 4.1 illustrates that indeed the reaction of NO$_3$ with aldehydes is an efficient heterogeneous reaction compared with other heterogeneous substrates. For the classes of organics studied, the following trend is observed: PAHs $>$ alkenoic acids $>$ aldehyde $>$ alcohols $>$ alkanoates. Assuming that the alkenoic acid reaction is due to the carbon-carbon double bond, this trend is roughly consistent with that of measured gas-phase rate constants of
NO$_3$ reactions at 298 K: $10^{-10}$–$10^{-13}$ for PAHs and alkenoic acids, $10^{-14}$–$10^{-15}$ for aldehydes, $10^{-15}$–$10^{-16}$ alcohols, and $10^{-16}$–$10^{-18}$ for alkanoates (all in units of cm$^3$ molecule$^{-1}$ s$^{-1}$).\textsuperscript{134}

Table 4.1: Comparison of reactive uptake coefficients for heterogeneous reactions involving solid organic substrates and NO$_3$ radical.$^a$

<table>
<thead>
<tr>
<th>Class</th>
<th>Chemical</th>
<th>T, K</th>
<th>Reactive Uptake Coefficient ($\gamma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycyclic Aromatic Hydrocarbons</td>
<td>Benz[a]anthracene</td>
<td>273–297</td>
<td>$1.0–66 \times 10^{-2}$ $^b$</td>
</tr>
<tr>
<td></td>
<td>Pyrene</td>
<td>273–297</td>
<td>$&gt;8.0 \times 10^{-2}$ $^{b,c}$</td>
</tr>
<tr>
<td></td>
<td>Fluoranthene</td>
<td>273–297</td>
<td>$&gt;2.0 \times 10^{-2}$ $^b$</td>
</tr>
<tr>
<td>Alkenoic Acid</td>
<td>Conjugated Linoleic Acid</td>
<td>263</td>
<td>$(8.0\pm3.0) \times 10^{-2}$ $^d$</td>
</tr>
<tr>
<td></td>
<td>Oleic Acid</td>
<td>268–283</td>
<td>$(5.3\pm1.1) \times 10^{-2}$ $^d$</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>Tridecanal</td>
<td>263</td>
<td>$(1.6\pm0.8) \times 10^{-2}$ $^e$</td>
</tr>
<tr>
<td>Alcohol</td>
<td>Glycerol</td>
<td>268–293</td>
<td>$(0.8–1.7) \times 10^{-3}$ $^d$</td>
</tr>
<tr>
<td>Alkanoate</td>
<td>Diethyl Sebacate (DES)</td>
<td>263–272</td>
<td>$(2.3–4.1) \times 10^{-4}$ $^d$</td>
</tr>
</tbody>
</table>

$^a$ Only $\gamma$ results from this laboratory group have been included and they have been ordered by decreasing $\gamma$ values. The only other report of $\gamma$ values for NO$_3$ uptake on pure organics is found in Moise et al.$^60$ and our results are generally similar to their $\gamma$ values except in the case of alkenoic acids (this is discussed in further detail in Gross et al.$^{64}$).

$^b$ Taken from Gross and Bertram.$^{67}$

$^c$ Taken from Mak et al.$^{93}$

$^d$ Taken from Gross et al.$^{64}$

$^e$ This study.

Figure 4.2 provides results for the uptake coefficient of NO$_3$ on binary liquid
mixtures containing the aldehyde. The uptake coefficients with 0 wt % tridecanal represent the reactions of NO$_3$ with pure matrix molecules (DES, DOS, and squalane). For all the matrix compounds studied, the addition of small amounts of tridecanal (<6 wt %) increased $\gamma$. Also, the increase depends on the type of matrix. For example, at approximately 4.5 wt % tridecanal, the reactive uptake coefficient in DES increased by a factor of 3 but in squalane the $\gamma$ value only increased by a factor of 1.4.

![Figure 4.2: Measured uptake coefficients of the NO$_3$ reaction with tridecanal in DES, DOS, and squalane matrices at 275 K.](image)

**4.3.2. Analysis of the Reactive Uptake Coefficient Data Using the Resistor Model**

To analyze the uptake results presented in Figure 4.2, we again used the resistor model. Similar to that in Section 3.3.3, if the reaction occurs in the bulk and the reactive uptake coefficient is not limited by the mass accommodation coefficient, then the following equation applies for the binary liquid mixtures:

$$ E \gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2 = \frac{(4H_{\text{matrix}}RT)^2 D_{\text{matrix}}^2 k_{2,\text{aldehyde}}^* M_{\text{aldehyde}}}{c_{\text{NO}_3}^2} $$

where $k_{2,\text{aldehyde}}^*$ is the bulk second-order rate constant for NO$_3$ reaction with the aldehyde,
and $M_{\text{aldehyde}}$ is the molarity of the aldehyde in each matrix (mol L$^{-1}$). According to E 4.1, a plot of $\gamma_{\text{mixture}}^{2} - \gamma_{\text{matrix}}^{2}$ against $M_{\text{aldehyde}}$ is expected to yield a straight line. Similar to that in Section 3.3.3, if the reaction occurs on the surface and assuming the reactive uptake coefficient is not limited by the adsorption coefficient, the following equation applies for the binary liquid mixtures:

$$E 4.2 \quad \gamma_{\text{mixture}} - \gamma_{\text{matrix}} = \frac{4H^{s}_{\text{matrix}} RTK^{s}_{\text{matrix}} k_{2^s,\text{aldehyde}}^{s}}{c_{\text{NO}_3}} M_{\text{aldehyde}}$$

where $k_{2^s,\text{aldehyde}}^{s}$ is the second-order rate constant for NO$_3$ reaction with the reactant at the surface.

If the reaction occurs at the surface and the assumptions outlined above are valid, then a plot of $\gamma_{\text{mixture}} - \gamma_{\text{matrix}}$ vs. $M_{\text{aldehyde}}$ is expected to yield a straight line. In Figure 4.3, in panels a–c, we have plotted $\gamma_{\text{mixture}}^{2} - \gamma_{\text{matrix}}^{2}$ vs. $M_{\text{aldehyde}}$ and in panels d–f, we have plotted $\gamma_{\text{mixture}} - \gamma_{\text{matrix}}$ vs. $M_{\text{aldehyde}}$. To evaluate the goodness-of-fit for the two different models (bulk and surface), we calculated $\chi^2$ values. The results from these calculations are included in Figure 4.3. Based on the $\chi^2$ values, kinetics for DOS and squalane mixtures are explained well by both the bulk and surface model. For DES, the kinetic data fit better to the surface model than the bulk model. To be conservative, below we use results from both models when estimating the lifetime of aldehydes in the atmosphere as well as making conclusions about the effect of the matrix on the NO$_3$–aldehyde organic reactions. It turns out that similar conclusions are reached regardless of the model used for interpreting the results.
Table 4.2 summarizes values of $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k^{2\circ,\text{aldehyde}}}$ and $H^S_{\text{matrix}}K^S_{\text{matrix}}k^{S,\text{aldehyde}}$ that were extracted from the kinetic measurements of NO$_3$ with tridecanal in the different matrices. It is interesting to note that the trend in $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k^{2\circ,\text{aldehyde}}}$ is in the order of DES > DOS > squalane. This trend is the same as that of $D_{\text{matrix}}$. 

Figure 4.3: Plots of $\gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2$ (panels a–c) and $\gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2$ (panels d–f) as a function of $M_{\text{aldehyde}}$. Panels a and d correspond to the reaction of NO$_3$ + tridecanal in DES, panels b and e correspond to the reaction of NO$_3$ + tridecanal in DOS, panels c and f correspond to the reaction of NO$_3$ + tridecanal in squalane. $R^2$ is the coefficient of determination for each linear fit.
Table 4.2: Calculated values of $H_{\text{matrix}} \sqrt{D_{\text{matrix}} k_{\text{2,aldehyde}}}^{2}$ and $H_{\text{matrix}}^S K_{\text{matrix}}^{S} k_{\text{2,aldehyde}}^{S}$ for the reactions of NO$_3$ with tridecanal in different matrices at 275 K

<table>
<thead>
<tr>
<th>Matrix</th>
<th>$H_{\text{matrix}} \sqrt{D_{\text{matrix}} k_{\text{2,aldehyde}}}^{2}$, cm M$^{0.5}$ atm$^{-1}$ s$^{-1}$</th>
<th>$H_{\text{matrix}}^S K_{\text{matrix}}^{S} k_{\text{2,aldehyde}}^{S}$, L cm$^{-2}$ atm$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DES</td>
<td>9.44 ± 2.47</td>
<td>14.43 ± 0.42</td>
</tr>
<tr>
<td>DOS</td>
<td>6.93 ± 2.29</td>
<td>12.43 ± 1.04</td>
</tr>
<tr>
<td>Squalane</td>
<td>3.65 ± 0.50</td>
<td>4.91 ± 0.64</td>
</tr>
</tbody>
</table>

$^a$ Error estimates obtained from 1σ standard deviations of each corresponding slope in Figure 4.3.

4.3.3. Reactive Uptake of N$_2$O$_5$ with Alcohols

Our previous study$^{64}$ showed that the uptake coefficient of N$_2$O$_5$ on liquid glycerol is >3.2×10$^{-4}$ and the heterogeneous reaction between N$_2$O$_5$ and alcohols may be potentially important in the atmosphere. In this study, we investigated the heterogeneous N$_2$O$_5$ reaction with four other organic reactants which all contain hydroxyl groups. Figure 4.4 provides the measured uptake coefficients of N$_2$O$_5$ reaction as well as the glycerol results for comparison.
Figure 4.4: Measured reactive uptake coefficients for reactions of N$_2$O$_5$ with liquid and solid polyalcohols as a function of temperature. Solid lines are meant to guide the eye and do not represent fits to the data. Dashed lines are used to show phase changes for the organics. The uptake coefficients for glycerol were obtained from Gross et al.$^{64}$

The N$_2$O$_5$ reactive uptake coefficient on PEG-300 was the largest ranging from $(1.5–1.9)\times10^{-2}$ while the smallest was on 1,2,6-trihydroxyhexane which was $<1.2\times10^{-4}$. The overall trend in the reactive uptake coefficients for all the liquid organics in reaction with N$_2$O$_5$ was PEG-300 $>$ PEG-400 $>$ glycerol $>$ (+)-diethyl L-tartrate $>$ 1,2,6-trihydroxyhexane.

For PEG-400, above 278 K the film was liquid and below this temperature the film was solid. A sharp decrease in the $\gamma$ value for the experiment below the freezing point of PEG-400 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 favorable for uptake and
reactivity.

4.3.4. Trend of N\textsubscript{2}O\textsubscript{5} Reactivity

The uptake coefficients of N\textsubscript{2}O\textsubscript{5} for single-component experiments varied by more than two orders of magnitude, which was surprisingly large. To try to rationalize these findings, we again used the resistor model of gas-liquid interactions.

If the reaction occurs in the bulk and the reactive uptake coefficient is not limited by the mass accommodation coefficient, the reactive uptake coefficient for a single-component alcohol can be explained with the following equation:

\[ E 4.3 \quad \gamma = \frac{4 R T H_{\text{alcohol}} \sqrt{D_{\text{alcohol}} k_{1^*,\text{alcohol}}}}{c_{N_{2}O_{5}}} \]

where \( \gamma \) is the reactive uptake coefficient of N\textsubscript{2}O\textsubscript{5} with the reactant, \( H_{\text{alcohol}} \) is the Henry’s law solubility constant of N\textsubscript{2}O\textsubscript{5} in the alcohol, \( D_{\text{alcohol}} \) is the diffusion coefficient for N\textsubscript{2}O\textsubscript{5} in the alcohol, \( k_{1^*,\text{alcohol}} \) is the bulk first-order rate constant for reaction of N\textsubscript{2}O\textsubscript{5} with the reactant, and \( c_{N_{2}O_{5}} \) is the mean molecular velocity of N\textsubscript{2}O\textsubscript{5}. According to E 4.3 the reactive uptake coefficient should be proportional to \( H_{\text{alcohol}} \sqrt{D_{\text{alcohol}} k_{1^*,\text{alcohol}}} \). Here we assume that the reaction rate constant \( k_{1^*,\text{alcohol}} \) is proportional to the concentration of hydroxyl groups in the liquid that could potentially react with N\textsubscript{2}O\textsubscript{5}. We use the “OH molarity” (moles of \(-\text{OH}\) groups L\textsuperscript{-1} of organic compound). Table 4.3 summarizes the viscosity (\( \eta \)), diffusion coefficient (\( D_{\text{alcohol}} \)), \textit{OH molarity}, the product of \( D_{\text{alcohol}} \) and \textit{OH molarity}, and the corresponding uptake coefficients at 293 K for N\textsubscript{2}O\textsubscript{5} with alcohols.
Table 4.3: Information pertaining to the discussion of the trend of N\textsubscript{2}O\textsubscript{5} uptake coefficients

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \eta ), cP</th>
<th>( D_{\text{alcohol}} )\textsuperscript{a} \text{ (cm}^2\text{ s}^{-1} )</th>
<th>( OH ) molarity \text{ (mol L}^{-1} )</th>
<th>( D_{\text{alcohol}} \times OH ) \text{ molarity} \text{ (cm}^2\text{ mol L}^{-1}\text{ s}^{-1} )</th>
<th>( \gamma ) at 293 K \text{ (cm}^2\text{ mol L}^{-1}\text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG-300</td>
<td>70</td>
<td>( 8.0\times10^{-8} )</td>
<td>7.5</td>
<td>( 5.8\times10^{-7} )</td>
<td>( 1.80\times10^{-2} )</td>
</tr>
<tr>
<td>PEG-400</td>
<td>90</td>
<td>( 6.0\times10^{-8} )</td>
<td>5.6</td>
<td>( 3.4\times10^{-7} )</td>
<td>( 9.20\times10^{-3} )</td>
</tr>
<tr>
<td>Glycerol</td>
<td>1500</td>
<td>( 3.6\times10^{-9} )</td>
<td>40.7</td>
<td>( 1.5\times10^{-7} )</td>
<td>( 6.45\times10^{-3} )</td>
</tr>
<tr>
<td>(+)-Diethyl L-Tartrate</td>
<td>N/A</td>
<td>N/A</td>
<td>11.7</td>
<td>N/A</td>
<td>( 5.17\times10^{-4} )</td>
</tr>
<tr>
<td>1,2,6-Trihydroxyhexane</td>
<td>2630</td>
<td>( 2.0\times10^{-9} )</td>
<td>24.8</td>
<td>( 5.0\times10^{-8} )</td>
<td>( 3\times10^{-4} )\textsuperscript{b}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The diffusion coefficient of a species in a liquid is related to the viscosity through the Stokes-Einstein equation \( D = k_b T (6 \pi \eta r)^{-1} \), where \( D \) is the diffusion coefficient, \( k_b \) is the Boltzmann constant, \( T \) is the temperature, \( \eta \) is the viscosity of the liquid, and \( r \) is the radius of the diffusing species. Here we have calculated the diffusion coefficient of N\textsubscript{2}O\textsubscript{5} in the alcohols based on their viscosity at 293 K. The radius of the N\textsubscript{2}O\textsubscript{5} particles was estimated as twice of the radius for O\textsubscript{3}. The radius of O\textsubscript{3} was obtained based on a recent modeling study.\textsuperscript{89}

\textsuperscript{b} This value was estimated from the \( \gamma \) value of 1,2,6-trihydroxyhexane at 278 K according to the general trend of uptake coefficients at different temperatures.

According to E 4.3, if we assume all the alcohols have similar \( H_{\text{alcohol}} \) values, the reactive uptake coefficient \( \gamma \) should be proportional to \( \sqrt{D_{\text{alcohol}} k_{1^\circ,\text{alcohol}}} \). Then plotting values of \( \gamma \) against \( \sqrt{D_{\text{alcohol}} \text{ (OH molarity)}} \) is expected to yield a straight line fit to the data.

If the reaction occurs at the surface and the reactive uptake coefficient is not limited by the adsorption coefficient, the reactive uptake coefficient can be explained...
with the following equation:

$$\gamma = \frac{4RT H^S_{alcohol} K^S_{alcohol} k^S_{1º,alcohol}}{c_{N_2O_5}}$$

where $H^S_{alcohol}$ is the surface Henry’s law constant, analogous to a Henry’s law equilibrium for the bulk condensed phase, $K^S_{alcohol}$ is an equilibrium constant linking the surface concentration to the bulk concentration of the organic liquid, and $k^S_{1º,alcohol}$ is the first-order rate constant for the $N_2O_5$ reaction with alcohol at the surface. At a fixed temperature (i.e., at 293 K), E 4.4 shows that the reactive uptake coefficient is proportional to $H^S_{alcohol} K^S_{alcohol} k^S_{1º,alcohol}$. We assumed that all the reactants here have similar $H^S_{alcohol} K^S_{alcohol}$ values and also that $k^S_{1º,alcohol}$ was proportional to the “OH molarity”. Then, for a surface reaction, plotting values of $\gamma$ against “OH molarity” is expected to yield a straight-line fit to the data.

In Figure 4.5, we plot the reactive uptake coefficient as a functions of $(D_{alcohol} \times OH \text{ molarity})^{0.5}$ (Panel a) and $OH \text{ molarity}$ (Panel b). Panel b shows that the surface model with the assumptions listed above cannot explain the data ($R^2 = 0.336$ and $\chi^2 = 295.80$). In contrast, Panel a shows that the reactive uptake coefficient is correlated with $(D_{alcohol} \times OH \text{ molarity})^{0.5}$ ($R^2 = 0.900$ and $\chi^2 = 9.03$). However the bulk model does not completely capture the trend in the data. This could be because the bulk model is not appropriate for some or all the alcohols studied and/or the assumptions discussed above (such as a single Henry’s law solubility for all the alcohols) are not appropriate. Regarding the former, it is interesting to note that for 1,2,6-trihydroxyhexane, the self diffusion coefficient is estimated on the order of $10^{-10}$ cm$^2$ s$^{-1}$ by using the Stokes-Einstein equation. This is in the range where calculations suggest that the transport of the condensed phase reactant can start to limit the overall uptake coefficient.\textsuperscript{132} This process is not included in the bulk model discussed above and may be, in part, why the bulk model does not accurately represent all the data.
We conclude that $\gamma$ does correlate with $(D_{\text{alcohol}} \times \text{OH molarity})^{0.5}$ but more work is needed with other alcohols to completely understand the dependence. It is likely that properties such as the Henry’s law solubility of the different alcohols, steric effects on the OH reaction rate constant, and transport of the alcohol within the condensed phase need to be considered.

In the next section, we use both the surface model and the bulk model to get an order of magnitude estimate of the atmospheric lifetime of the alcohols. The conclusions regarding the lifetime do not depend strongly on the model used.
4.4. Atmospheric Implications

4.4.1. Lifetime of Aldehyde due to NO₃ Oxidation

Next we use the kinetic parameters measured above for the mixtures, to estimate the lifetime of an aldehyde in the troposphere. If the reaction occurs in the bulk then the following equation⁶⁹,¹²⁹,¹³⁰ can be used together with parameters shown in Table 4.2 to estimate the lifetime:

\[
E 4.5 \quad \sqrt{[\text{aldehyde}]} = \sqrt{[\text{aldehyde}]_0} - \frac{3P_{\text{NO}_3} H_{\text{matrix}} D_{\text{matrix}} k_{2^\circ,\text{aldehyde}}}{2r_{\text{particle}}} t
\]

where \([\text{aldehyde}]\) is the concentration of an aldehyde at time \(t\), \([\text{aldehyde}]_0\) is the initial concentration of the aldehyde in the particle.

If the reaction occurs at the surface then the following equation together with parameters in Table 4.2 can be used to estimate the lifetime of an aldehyde in the atmosphere:

\[
E 4.6 \quad \ln \left( \frac{[\text{aldehyde}]}{[\text{aldehyde}]_0} \right) = - \frac{3P_{\text{NO}_3} H_{\text{matrix}} k_{\text{alcohol}} k_{2^\circ,\text{aldehyde}}}{r_{\text{particle}}} t
\]

Table 4.4 shows the estimated lifetime of an aldehyde calculated using kinetic parameters determined with aldehyde in different matrices at 275K and using an NO₃ mixing ratio of 25 ppt. Several conclusions can be drawn from the data available in Table 4.4. A comparison of the calculated bulk and surface cases reveals that the lifetimes differ by only a factor of 2. This is a reasonably small effect upon consideration of the uncertainties that arise when extrapolating laboratory data to the atmosphere (e.g., particle composition). When making the comparison between the different matrices studied, the lifetimes differ by a factor of 2–3. This is also reasonably small. Finally, regardless of the matrix or the assumption of liquid vs. bulk dominance, all calculated lifetimes are short (i.e., all <8 h). One can thus conclude that the lifetime of aldehydes similar to tridecanal is likely short in the atmosphere if the NO₃ concentrations are >25 ppt, the particle matrix is in the liquid state, and the diffusion coefficient of the aldehyde...
in the matrix is greater than $10^{-10}$ to $10^{-15}$ cm$^2$ s$^{-1}$. At smaller diffusion coefficients, the reactive uptake can be limited by the diffusion of the aldehyde in the particle. As a result, different equations other than E 4.5 and E 4.6 would be used to calculate the lifetime of the particle. \(^{69,119,132}\)

**Table 4.4: Estimates of the atmospheric lifetimes of aldehyde-containing organics aerosol particles, $\tau_{\text{aldehyde}}$, using parameters determined from uptake experiments with tridecanal in different matrices (DES, DOS, and squalane).**

<table>
<thead>
<tr>
<th>System Used for Determining Kinetic Parameters</th>
<th>$\tau_{\text{aldehyde}}$, h (a)</th>
<th>Assuming a Bulk Mechanism</th>
<th>Assuming a Surface Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tridecanal in DES</td>
<td>1.90</td>
<td>2.56</td>
<td></td>
</tr>
<tr>
<td>Tridecanal in DOS</td>
<td>1.98</td>
<td>2.96</td>
<td></td>
</tr>
<tr>
<td>Tridecanal in Squalane</td>
<td>3.60</td>
<td>7.54</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) When calculating the atmospheric lifetime it was assumed that the mole fraction of the aldehydes in the particle was 0.1 and that the particle diameter was 200 nm.

**4.4.2. Lifetime of Alcohols due to N\(_2\)O\(_5\) Oxidation**

Here we assume the reaction of N\(_2\)O\(_5\) with alcohols should follow either a bulk mechanism or a surface mechanism. Equations analogous to E 4.1, E 4.2, E 4.5 and E 4.6 were used to calculate $H_{\text{alcohol}}\sqrt{D_{\text{alcohol}}k_{2^\circ,\text{alcohol}}}$ values, $H_{\text{alcohol}}K_{\text{alcohol}}^S k_{2^\circ,\text{alcohol}}^S$ values, and atmospheric lifetimes for alcohols. Table 4.5 summarizes the calculated $H_{\text{alcohol}}\sqrt{D_{\text{alcohol}}k_{2^\circ,\text{alcohol}}}$ and $H_{\text{alcohol}}K_{\text{alcohol}}^S k_{2^\circ,\text{alcohol}}^S$ values and the estimated atmospheric lifetimes of different pure alcohol particles due to N\(_2\)O\(_5\) oxidation. An N\(_2\)O\(_5\) concentration of 1 ppb was used in these calculations, roughly corresponding to moderately polluted levels. \(^{131}\)
<table>
<thead>
<tr>
<th>Compound</th>
<th>$H_{alcohol} \sqrt{D_{alcohol} k_{2^*,alcohol}}$ (cm M$^{0.5}$ atm$^{-1}$ s$^{-1}$)</th>
<th>$\tau$, h $^b$</th>
<th>$H_{alcohol} S_{alcohol} k_{2^*,alcohol}^S$ (L cm$^{-2}$ atm$^{-1}$ s$^{-1}$)</th>
<th>$\tau$, h $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG-300</td>
<td>2.18</td>
<td>0.65</td>
<td>1.13</td>
<td>0.82</td>
</tr>
<tr>
<td>PEG-400</td>
<td>1.29</td>
<td>0.95</td>
<td>0.75</td>
<td>1.24</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.41</td>
<td>6.50</td>
<td>0.11</td>
<td>8.34</td>
</tr>
<tr>
<td>(+)-Diethyl L-Tartrate</td>
<td>0.05</td>
<td>35.2</td>
<td>0.02</td>
<td>44.1</td>
</tr>
<tr>
<td>1,2,6-Trihydroxyhexane</td>
<td>0.02</td>
<td>104.7</td>
<td>0.007</td>
<td>130.4</td>
</tr>
</tbody>
</table>

$^a$ Calculations of atmospheric lifetimes were performed under the assumptions of pure alcohol with a diameter of 200 nm.

$^b$ Lifetime estimates where reactions dominated by the bulk mechanism are assumed.

$^c$ Lifetime estimates where reactions dominated by the surface mechanism are assumed.

Several conclusions can be drawn from Table 4.5. First, comparing the calculations assuming bulk with the calculations assuming surface, the lifetimes only differ by a factor of 1.3 which is a small effect. Second, the lifetime of alcohols with respect to N$_2$O$_5$ can be very short, consistent with initial work based on glycerol. Third, the lifetime of alcohols with respect to N$_2$O$_5$ can also be long, depending on the physical and chemical properties of the organic liquid. As a result, one should be careful when applying the uptake results of one molecule to a whole class of compounds. Details such as steric effects, Henry’s law solubilities, and transport of the reactant in the liquid all need to be considered. With this in mind, one should also be cautious when applying our tridecanal or methyl oleate results discussed above liberally to all aldehydes and unsaturated organics. Studies with other aldehydes and other unsaturated organics are also needed.
5 Conclusions

5.1. Summary of Work

The overall goal of this thesis was to increase the understanding of atmospherically important heterogeneous reactions. This was achieved through investigations of the reactions of NO₃ and N₂O₅ with organics in the condensed phase. Different classes of organic substrates were chosen as representatives of organic aerosol components that are found in the atmosphere. The kinetics of the NO₃ reaction with pure alkenoic acids, alkanes, and alkanoates and of the N₂O₅ reaction with alcohols was studied here. This work also focused on the heterogeneous reactions of NO₃ with two-component organic mixtures. From the kinetics results, the atmospheric lifetimes for different organic substrates were estimated.

In Chapter 3, the reactive uptake coefficients of NO₃ with pure organic substrates were determined. These data agree with previous studies in that NO₃ reacts much faster with unsaturated organics than with saturated organics. Based on these results, we further investigated the kinetics of NO₃ with three different liquid mixtures: methyl oleate in DES, DOS, and squalane. The reactive uptake coefficients of the mixtures increase significantly when adding small amounts of methyl oleate (<4%). The increase can vary by a factor of 5 depending on the matrix compounds used. The kinetics of solid-liquid mixtures was also investigated with the uptake coefficient decreased by a factor of 10 after exposure to NO₃ for 90 minutes. Based on the uptake results, the atmospheric lifetimes of unsaturated substrates in binary liquid mixtures were estimated to be short (< 35 mins). Whereas, for a semisolid mixture, a lower limit to the lifetime was estimated to be 1-2 hours.

In Chapter 4, two-component systems were further investigated. Specially NO₃ uptake on binary mixtures containing tridecanal were studied. This study showed that uptake coefficients for the mixtures increased with the addition of tridecanal (< 6%), and a dependence on the type of matrix was also observed here. This work also showed that the reactivity of alkanals with NO₃ is higher than for saturated organics but lower than for
unsaturated compounds. The lifetimes of alkanals in the atmosphere due to NO\textsubscript{3} oxidation were also calculated and they ranged from 2 to 8 hours. This chapter also provided the kinetics results of experiments concerning the uptake of N\textsubscript{2}O\textsubscript{5} by alcohols, where uptake coefficients ranged from $8 \times 10^{-5}$ to $2 \times 10^{-2}$. To explain this wide range of $\gamma$ values, we used the resistor model. We showed that $\gamma$ correlated with $(D_{\text{alcohol}} \times OH \text{ molarity})^{0.5}$, but more work is needed to complete understand the dependence. The estimated lifetimes of alcohols due to N\textsubscript{2}O\textsubscript{5} reaction lied within a wide range, from about 40 min to over 4 days.

5.2. Consideration of Future Work

In Chapter 3 and 4, we conclude that the lifetimes of unsaturated organics and aldehydes are likely to be short in the atmosphere based on the kinetics results in our study. For future work, it would be good to choose reactants and matrices that cover a wider range of the physical properties such as the diffusion coefficient or the Henry’s law solubility constant.

All of the NO\textsubscript{3} heterogeneous reactions performed in this work involved the use of two-component mixtures. As discussed in Chapter 1, real atmospheric aerosols are supposed to be much more complex systems. Future work could increase the complexity of organic mixtures in order to better mimic atmospheric aerosols. Another way of increasing the complexity and of moving more toward realistic aerosols would be to further investigate multiphase systems. These reactions have been investigated with other oxidants such as O\textsubscript{3} and OH radicals but little work has been done with respect to NO\textsubscript{3}.

This work has focused on the kinetics of NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} reactions. Future work might involve the investigation of the mechanisms and the products of these reactions since nitrogenated products could potentially be toxic substrates. Only preliminary work has been done on the NO\textsubscript{3} reaction mechanism\textsuperscript{67} and a more in-depth study is needed to confirm the actual reaction steps, elucidate the branching ratios of the different reaction paths, and to make conclusive statements about the reaction products.
References

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Appendix

A1. Derivation of E 3.1 in Chapter 3.3.3.

According to the resistor model, if the reaction occurs in the bulk, and if NO₃ can react with both methyl oleate and the matrix molecules, and if the reactive uptake coefficient is not limited by the mass accommodation coefficient (i.e., α >> γ, where α is the mass accommodation coefficient) then the following equation applies for our binary liquid mixtures (see Chapter 2.3 for a discussion on the resistor model and the application of the resistor model to pure liquids (i.e. one reactive component)): 68, 135, 136

\[ \gamma_{\text{mixture}} = \frac{4H_{\text{mixture}}RT \sqrt{D_{\text{mixture}}(k_{\text{matrix}}M_{\text{matrix}} + k_{\text{oleate}}M_{\text{oleate}})}}{c_{\text{NO}_3}} \]

where \( H_{\text{mixture}} \) corresponds to the Henry’s law solubility constant of NO₃ in the mixture, \( D_{\text{mixture}} \) corresponds to the diffusion coefficient for NO₃ in the mixture, \( k_{\text{matrix}} \) is the second-order rate constant for the NO₃ reaction with matrix molecules, and \( M_{\text{matrix}} \) is the molarity of the matrix molecules in the mixture.

In this study, the amount of the reactant (methyl oleate) is always small (wt% < 4%) in the mixture. As the Henry’s law solubility constant and the diffusion coefficient of NO₃ in the mixture is approximately the same as the Henry’s law solubility constant and the diffusion coefficient of NO₃ in pure matrix molecules (i.e. \( H_{\text{mixture}} \approx H_{\text{matrix}} \) and \( D_{\text{mixture}} \approx D_{\text{matrix}} \)) where \( H_{\text{matrix}} \) is the Henry’s law solubility constant of NO₃ in the pure liquid of matrix molecules, and \( D_{\text{matrix}} \) is the diffusion coefficient of NO₃ in the pure liquid of matrix molecules). Substituting these approximations into A1.1 results in the following equation.

\[ \gamma_{\text{mixture}}^2 = \frac{(4H_{\text{matrix}}RT)^2 D_{\text{matrix}} k_{\text{matrix}} M_{\text{matrix}}}{c_{\text{NO}_3}^2} + \frac{(4H_{\text{matrix}}RT)^2 D_{\text{matrix}} k_{\text{oleate}} M_{\text{oleate}}}{c_{\text{NO}_3}^2} \]

For our study \( \gamma_{\text{mixture}}^2 \) varies at least by a factor of 5, but \( M_{\text{matrix}} \) only varies by 3%. Hence we assume that the first term in equation A1.2 is constant and equal to \( \gamma^2 \) for a pure liquid of matrix molecules. We refer to this as \( \gamma_{\text{matrix}}^2 \) which can be calculated from the \( \gamma \) value in Table 3.1. After making this assumption and substitution we have the
A1.3 \[ \gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2 = \frac{(4H_{\text{matrix}}RT)^2 D_{\text{matrix}} k_{\text{oleate}} M_{\text{oleate}}}{c_{\text{NO}_3}^2} \]

A1.3 is equivalent to E 3.1 in chapter 3.3.3. A similar equation to E 3.1 was used to describe the uptake coefficient of NO\(_3\) on an aqueous solution that had two parallel bulk reactions: a reaction with water and a reaction with ions. \(^{135,136}\)
A2. Derivation of E 3.2 in Chapter 3.3.3.

According to the resistor model, if NO$_3$ can react with both methyl oleate and the matrix molecules at the surface and the reactive uptake coefficient is not limited by the adsorption coefficient (i.e., $\alpha >> S$, where S is the adsorption coefficient) then the following equation applies for our binary liquid mixtures (see Chapter 2.3 for a discussion on the resistor model and the application of the resistor model to pure liquids (i.e. one reactive component)).$^{68, 69, 137}$

\[
A2.1 \quad \gamma_{mixture} = \frac{4RTH^S_{mixture}K^S_{mixture}(k^S_{matrix}M_{matrix} + k^S_{oleate}M_{oleate})}{c_{NO_3}}
\]

Employing approximations similar to the ones used to derive A1.2 above, we derive equation A2.2 below.

\[
A2.2 \quad \gamma_{mixture} = \frac{4RTH^S_{matrix}K^S_{matrix}k^S_{matrix}M_{matrix}}{c_{NO_3}} + \frac{4RTH^S_{matrix}K^S_{matrix}k^S_{oleate}M_{oleate}}{c_{NO_3}}
\]

Employing approximations similar to the ones used to derive A1.3 above, we derive equation A2.3:

\[
A2.3 \quad \gamma_{mixture} - \gamma_{matrix} = \frac{4RTH^S_{matrix}K^S_{matrix}k^S_{oleate}M_{oleate}}{c_{NO_3}}
\]

A2.3 is equivalent to E 3.2 in Chapter 3.3.3.