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Photoelectron Resonance Capture Ionization Aerosol Mass Spectrometry of Organic Particulate Matter

James Zahardis

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PHOTOELECTRON RESONANCE CAPTURE IONIZATION AEROSOL MASS SPECTROMETRY OF ORGANIC PARTICULATE MATTER

A Dissertation Presented

by

James Zahardis

to

The Faculty of the Graduate College

of

The University of Vermont

In Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy Specializing in Chemistry

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Accepted by the Faculty of the Graduate College, The University of Vermont, in partial fulfillment of the requirements for the degree of Doctor of Philosophy specializing in Chemistry.

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ABSTRACT

Organic aerosols are ubiquitous to the lower atmosphere and there is growing concern about their impact on climate and human health. These aerosols typically have multicomponent compositions that change over time in part due to oxidation by reactive trace gases, such as ozone. A current challenge to the atmospheric research community is to develop better methods of analysis of these particles. Photoelectron resonance capture ionization aerosol mass spectrometry (PERC I-AMS) is an online mass spectrometric method that has been applied to the analysis of organic aerosols. One of its key advantages is that it employs low energy (~ 0 eV) photoelectrons in the ion forming process, which has been shown to minimize fragmentation in the organic analytes, thus simplifying mass spectral interpretation.

This dissertation focuses on the application of PERC I-AMS to the analysis of organic particles. Initial emphasis is placed on the heterogeneous reaction of gas phase ozone with liquid oleic acid particles. Products identified included carboxylic acids, aldehydes, and peroxides including alpha-acyloxyalkyl hydroperoxides polymers. The evidence of peroxidic products suggested the stabilization of carbonyl oxide intermediates (i.e. Criegee intermediates) that are formed during ozonolysis. Subsequent PERC I-AMS experiments investigated the reactivity of the stabilized Criegee intermediates. This included investigating the reaction of Criegee intermediates with unsaturated fatty acids and methyl esters. A novel ketone-forming reaction is described in these systems, suggesting the Criegee intermediates can react at a carbon-carbon double bond. Further PERC I-AMS experiments investigated the oxidative processing of particulate amines including octadecylamine and hexadecylamine. Ozonolysis of these amines resulted in strong NO₂⁻ and NO₃⁻ ion signals that increased with the ozone exposure and suggested a mechanism of progressive oxidation. Additionally, a strong ion signal was detected for NO₃⁻(HNO₃), which is the ion core of the most important ion cluster series in the troposphere, NO₅⁻(HNO₃)ₙ(H₂O)ₘ. PERC I-AMS was applied to the analysis of ozonized mixed particles of amines with oleic acid or dioctyl sebacate. In the ozonolysis of the amines with oleic acid, products included imines and amides. The routes to the amides were shown to most likely arise from the reactivity of stabilized Criegee intermediates and/or secondary ozonides with the amines. There was also direct evidence of the formation of a surface barrier in the octadecylamine and oleic acid reaction system, which resulted in the retention of oleic acid at high ozone exposures.

These experiments have fostered a better understanding of the analytical capacity of PERC I-AMS in assaying the reactivity of organic aerosols as well as giving a more accurate description of the heterogeneous chemistry of these challenging reaction systems. Suggestions for adaptations to PERC I-AMS and future experiments on heterogeneous oxidative processing of organic aerosols form the conclusion of this work.
CITATIONS

Material from this dissertation has been published in the following form:


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1. INTRODUCTION

1.1. Overview of the Atmosphere

The emphasis of this introduction is on the chemistry of aerosols of the lowermost stratum of the atmosphere, namely the troposphere; however a very brief description of the atmospheric system as a whole is presented as an overview. Special attention is given to organic aerosols which are the focus of the research presented in subsequent chapters.

The lowermost layer of the atmosphere is the troposphere, which is characterized by a general decrease in temperature with an increase in altitude. The troposphere is the thinnest layer of the atmosphere, extending from the Earth’s surface to a typical altitude of 10 – 12 km \(^1,^2\). This layer is also characterized by a rapid vertical mixing of air, such that heated air can rise from the surface of the Earth to the boundary of the troposphere and stratosphere (i.e. the tropopause) within a few days or less. The troposphere is the most important atmospheric layer in the Earth’s hydrological cycle with almost all the atmospheric water vapor and water in the form of hydrometeors (i.e. ice, fog, rain and clouds) found there\(^1-^3\). As will be discussed in following sections, the troposphere has the highest content of organic aerosols, which is the focus of the research presented herein.
Above the tropopause is the stratosphere which, opposite to the troposphere, has an increase in temperature with altitude. This layer extends from the tropopause to a height of about 45 – 55 km \(^1,^2\) and has a slow rate of vertical mixing compared to the troposphere. Central to the chemistry of the stratosphere is the Chapman cycle \(^1,^4\) which maintains the steady state concentration of ozone in this stratum:

\[
\begin{align*}
(1.1) \quad O_2 + h\nu & \rightarrow 2 O \\
(1.2) \quad O + O_2 & \rightarrow O_3 \\
(1.3) \quad O + O_3 & \rightarrow 2 O_2 \\
(1.4) \quad O_3 + h\nu & \rightarrow O + O_2
\end{align*}
\]

The last of these reactions is arguably one of the most important chemical reactions on Earth for the preservation of life – ozone (O\(_3\)) strongly absorbs ultraviolet radiation with wavelengths lower than 290 nm \(^5-^7\), with the shorter wavelength radiation being noted for damaging DNA and subsequently being mutagenic \(^8,^9\). It should also be noted that the filtration of the shorter wavelength radiation in the ozone layer of the stratosphere dictates the wavelengths of radiation that reaches the troposphere (\(\lambda > 290\) nm, commonly called actinic radiation). Hence the photochemistry that will be noted in the following subsection on tropospheric chemistry occurs essentially at wavelengths greater than 290 nm.

The lower atmosphere is commonly defined as the troposphere and the stratosphere, while the layers above that, namely the mesosphere, thermosphere and exosphere are referred to as the upper atmosphere. The mesosphere extends from the top of stratosphere (i.e. the stratopause) to about 80 – 90 km, has a decrease in temperature
with altitude and, like the troposphere, and is characterized by rapid vertical mixing \(^1\), \(^{10}\). It is the coldest region of the atmosphere with temperatures having a lower temperature limit of approximately \(-100\, ^\circ \text{C}\) \(^1\), \(^{10}\). Conversely the layer above the mesosphere, the thermosphere, is the hottest layer of the atmosphere with temperatures increasing with altitude and exceeding \(2000\, ^\circ \text{C}\) \(^{11}\). This layer extends from the uppermost layer of the mesosphere to about 100 km altitude. It should be noted that the upper mesosphere and the lower to mid thermosphere are often delineated as the ionosphere since this region is characterized by the photoionization of atoms and small gas phase molecules making this layer the most ionized component of the Earth’s atmospheric system \(^{12}\). Above the thermosphere is the exosphere, which extends to about 500 km altitude. This layer is characterized by the presence of light gases, such as hydrogen and helium, with sufficient kinetic energy to escape from the Earth’s gravitational field into space.

### 1.2. Oxidants of the Troposphere with Emphasis on Ozone

In the following subsection emphasis will be placed upon the generation of important gas phase oxidants. Special attention will given to ozone since the reactivity of this trace oxidant with lipids is the emphasis of the research presented herein. Details of the reactions of ozone with organics will be presented in the final sections of the introduction which focus on the ozonolysis of unsaturated organic molecules.

Most molecular species emitted from the surface of the Earth are oxidized and/or react photochemically in the troposphere \(^1\), \(^4\). The majorities of organic species are
oxidized directly by a variety of nitrogen oxides or are oxidized by one of the products stemming from the photolysis of nitrogen oxides\textsuperscript{13-15}. One of the most important oxidants arising from photolysis of nitrogen oxides is ozone. Unlike the stratosphere where ozone is generated exclusively via the photochemistry of oxygen (i.e. O and O\textsubscript{2}) as described by the Chapman cycle, the most important source of tropospheric ozone involves the photochemistry of NO\textsubscript{2} and NO (collectively deemed NO\textsubscript{x})\textsuperscript{16,17}:

\begin{align*}
(1.5) \text{NO}_2 + h\nu \ (\lambda \geq 420 \text{ nm}) & \rightarrow \text{NO} + \text{O}(^3\text{P}) \\
(1.6) \text{O}(^3\text{P}) + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} \\
(1.7) \text{O}_3 + \text{NO} & \rightarrow \text{NO}_2 + \text{O}_2
\end{align*}

The M in 1.6 denotes a third molecular body, typically N\textsubscript{2} or O\textsubscript{2} that stabilizes the ozone by absorbing vibrational energy. The ozone steady-state (SS) concentration can readily be shown to be directly proportional to NO\textsubscript{2} and inversely proportional to NO\textsuperscript{16,17}:

\[
[\text{O}_3]_{ss} \propto \frac{[\text{NO}_2]}{[\text{NO}]},
\]

While most ozone in the troposphere stems from NO\textsubscript{x} chemistry a small amount of ozone originates from periodic intrusions of the stratosphere into the troposphere\textsuperscript{18} and also reactions of volatile organic compounds (VOC) with NO\textsubscript{x}\textsuperscript{4,13,15,17}.

The most significant sources of NO\textsubscript{x} are anthropogenic emissions (i.e. pollution), with emissions from combustion in motor vehicle engines being the most
important specific source\textsuperscript{19-22}, consequently the concentrations of ozone in the polluted urban and suburban troposphere is usually greater than in rural and remote regions. For comparison, typical concentrations of ozone in rural and remote regions is less than 10 ppbv while in polluted urban regions the concentration can exceed 100 ppbv\textsuperscript{1, 21, 29}. Episodic summertime daily ozone levels of over 500 ppbv have been measured in some of the most polluted cities such as Los Angeles\textsuperscript{21, 29}.

Ozone is the precursor to another important oxidant, the nitrate radical (NO\textsubscript{3})\textsuperscript{1, 14}:

\begin{equation}
\text{(1.8) } \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2
\end{equation}

Although this reaction occurs both during the day and nighttime hours, during the day NO\textsubscript{3} rapidly undergoes photolysis. In this context the nitrate radical is an unusual tropospheric oxidant in that it absorbs actinic radiation very strongly into the red\textsuperscript{14}. Most of the other tropospheric oxidants, including ozone, have strong absorption bands in the ultraviolet region of the spectrum and absorb weakly in the visible region\textsuperscript{13, 16}. The photolysis of NO\textsubscript{3} has two possible pathways\textsuperscript{1, 14}:

\begin{align}
(1.9) \text{NO}_3 + \text{h} \nu & \rightarrow \text{NO}_2 + \text{O}(^3\text{P}) \\
(1.10) \text{NO}_3 + \text{h} \nu & \rightarrow \text{NO} + \text{O}_2.
\end{align}
The highest quantum yield of Reaction (1.9) at 298 K is at 585 nm with a yield of 0.983 and for Reaction (1.10) it is at 595 nm with a yield of 0.359\textsuperscript{14}. The diurnal lifetime of the nitrate radical is relatively short and is inversely proportional to the relative humidity. For example, the calculated atmospheric lifetime, $\tau$, of NO$_3$ in very dry locations is up to 60 min., such as Death Valley (California), where typical relative humidity is 20% or less, while for relative humidity 80% the atmospheric lifetime is usually less than 3 min\textsuperscript{14}. Hence, at this time, NO$_3$ is only considered an important oxidant in the nighttime troposphere\textsuperscript{1,14}.

The nitrate radical is a ubiquitous oxidant but in terms of reactivity with organic molecules they can be generalized into two broad categories of reaction: hydrogen abstraction and addition to unsaturated (i.e. double and triple) carbon-carbon bonds\textsuperscript{13,14}. The first of these general reactions represents an important source of nitric acid to the nighttime troposphere\textsuperscript{14,23}:

\[(1.11) \ NO_3 + RH \rightarrow HNO_3 + R.\]

In Reaction (1.11) R denotes an alkyl or aryl group and on the right hand side of this equation is a free radical. The second of these generalized reactions includes reactions that lead to the formation of alkyl nitrates\textsuperscript{14,24,25}, $R_1R_2(NO_2)R_3R_4$, where $R_1$ – $R_4$ denote hydrogen, alkyl, and/or aryl groups, and may be equivalent. The products, alkyl nitrates, are a source of NO$_2$ via both thermal and photochemically induced decomposition\textsuperscript{4,26}, and represent a sink for reactive nitrogen in the troposphere. Further
chemistry involving NO$_3$ will be discussed in Chapter 5 of this work in the context of the oxidation of amine aerosols.

The other important oxidant of the troposphere is the hydroxyl radical, OH, and its chemistry is intimately related to ozone. Most sources of OH are photolytic, including the photolysis of ozone, which is a source of OH$^{16,27}$:

\begin{align*}
(1.12) \ O_3 + h\nu (\lambda \leq 336 \text{ nm}) \rightarrow O(^1D) + O_2 \\
(1.13) \ O(^1D) + H_2O \rightarrow 2 \ OH \\
(1.14) \ O(^1D) + M \rightarrow O(^3P) + M.
\end{align*}

As described previously, M is typically N$_2$ or O$_2$. Also note that the formation of OH in Reaction (1.13) is a function of the relative humidity (RH). For example, at 50% RH (300 K and sea level) there is approximately a 10% conversion of O(^1D) to OH, with the remainder of O(^1D) deactivating via Reaction (1.14)$^{27}$. The above reaction sequence is probably the most important source of OH in the rural and remote troposphere, and contributes to the OH load in the polluted troposphere as well$^{4,16,27}$. However, in the urban troposphere the photolysis of many molecular species associated with anthropogenic emissions lead to OH generation, with perhaps the most important being the photolysis of nitrous acid (HONO), a common gas phase species in polluted environments$^{28,29}$:

\begin{align*}
(1.15) \ \text{HONO} + h\nu (\lambda < 400 \text{ nm}) \rightarrow \ OH + \text{NO}.
\end{align*}
The hydroxyl radical is probably the most ubiquitous oxidant in the troposphere with two broad general modes of reactivity with organic molecules in the gas phase, namely hydrogen abstraction and β-scission\textsuperscript{13, 15, 30, 31}. While there is a good body of experimental data on its gas phase reactivity \textsuperscript{13, 15, 30, 31} there is far less data on its heterogeneous reactivity on organic aerosols\textsuperscript{32} and other highly interfacial systems, such as films\textsuperscript{33-35}. As shall be discussed in Chapter 6, the limited number of fundamental laboratory studies in OH reactivity with organic aerosols stems mainly from difficulties in quantifying OH concentrations\textsuperscript{36-38} and monitoring product evolution\textsuperscript{35, 39}.

1.3. Introduction to the Aerosols of the Lower Atmosphere

The focus of the following subsection is to introduce terms, definitions, and conventions associated with aerosol chemistry and physics that will be referred to throughout the remainder of this work. Emphasis will be placed on size and composition categorizations of aerosols and key implications of atmospheric particulate, with special attention given to organic aerosols.

Aerosols are liquid, solid or semi-solid suspensions in a gas, ubiquitous to both the stratosphere and troposphere and are present in remote, rural, and urban environments with concentrations\textsuperscript{4} as high as $10^7$ to $10^8$ cm\textsuperscript{-3}. In the context of atmospheric chemistry and physics the terms particles, particulate matter or simply particulate are generally
A common way to characterize aerosols is by size, which varies widely with particles having diameters ranging from approximately 0.002 to 100 \( \mu \text{m} \); however, these limits are loosely defined. For example, at the lower size limit there is ambiguity between where a cluster becomes an aerosol. Similarly at the higher end size limit there is ambiguity in defining when an aerosol becomes a hydrometeor such as a water droplet or, for a solid, the delineation between particulate and a grain. In this document we will use terminology most commonly used with the prevalent current texts\(^1,4\) on atmospheric chemistry and recent reviews\(^40-42\) on aerosols in the lower atmosphere.

In terms of size, particles are defined into two broad categories (i.e. modes): fine and coarse particles. Coarse mode particles have a diameter of about 2 \( \mu \text{m} \) or greater. Most particles in this mode are generated by frictional forces such as grinding, wind, and erosion. Common sources of coarse particles include fugitive dust\(^43-45\), sea salt sprays\(^46,47\), and volcanic emissions\(^48,49\). Most biological particles that are composed of whole and fragmented cellular material such as bacteria\(^50,51\), spores\(^50\), pollen\(^52,53\), fungi\(^51\), and plant detritus\(^54\) are in the coarse mode. Similarly, soot particles, which are very important aerosols in terms of human health impact\(^55,56\) and climatology\(^57-59\), are typically found in the coarse mode. Note that while biological and soot particles are carbonaceous they are usually not defined as organic aerosols.

Coarse particles have some properties that should be noted before proceeding to fine particles which are the emphasis of this work. Most coarse particles are removed
from the atmosphere rapidly by gravitational settling or by wet deposition (washout), which are generally termed sedimentation. Sedimentation is countered by reentrainment by wind as well as by electrostatic forces that can be of similar order of magnitude as gravitational forces for coarse particles, especially on ice particles generated in ice storms and mineral dusts generated in sandstorms. Similarly, episodic events can transport dust and other coarse particles globally, as has been documented with Saharan and Asian dusts originating from sandstorms. Other features of coarse range particles will be discussed in the following sections on the implications of aerosols in the lower atmosphere.

The other broad size distribution is the fine mode with an upper limit of 2 μm to a lower limit of about 0.002 μm. This mode is commonly divided into three size ranges: the accumulation range (~0.1-2 μm), the transient nuclei range (or Aitken range ~0.01-0.1 μm), and ultra fine particle range (~0.002-.01 μm).

Particles in the accumulation range are generally formed by thermo-chemical conversion of gas phase molecules to lower volatility vapors, then homogeneous nucleation, followed by condensation growth of these nuclei. These nuclei can continue to grow, including by further condensation of low volatility vapors on their surface and eventually form small droplets. Accumulation range particles can also form from coagulation of smaller particles as well, typically aerosols in the Aitken range. These droplets are typically removed from the atmosphere by wet deposition. Since most accumulation range particles originate from low volatility gas phase species, they are closely associated with combustion processes which are important sources of
these vapors. Subsequently, particles in this range are far richer in organics than coarse particles \textsuperscript{1, 4, 40, 41}. However accumulation range particles are an important atmospheric sink of common inorganic molecular ions\textsuperscript{70-72}, including the ammonium ion (NH\textsubscript{4}\textsuperscript{+}), nitrate ion (NO\textsubscript{3}\textsuperscript{−}), and sulfate ion (SO\textsubscript{4}\textsuperscript{2−}). Many of the studies presented in this dissertation investigate organic particles that are in the accumulation range.

Combustion processes are sources of both accumulation range and Aitken range particles \textsuperscript{73, 74}. While dirty flames (i.e. incomplete combustion) have been shown to be a significant source of accumulation range particles, cleaner flames tend to favor the Aitken range \textsuperscript{75}. Aitken range particles are of central importance to cloud chemistry \textsuperscript{76-79}. Since they are typically generated under high-temperature conditions, fresh Aitken range particles are typically hygroscopic \textsuperscript{77, 79}. As a function of the relative humidity these particles can undergo reversible hygroscopic growth with water and be taken up into cloud and fogs. Within the cloud and fog the hydrated particles can undergo host of photochemical, oxidation, and acid-base reactions, with a notable case being the uptake and oxidation of sulfur dioxide (SO\textsubscript{2}) to sulfate (i.e. SO\textsubscript{2} conversion) \textsuperscript{4, 80}. Under these circumstances the particle becomes sulfate enriched, grows and can be deposited back to ground level which is central to the global sulfur geochemical cycle\textsuperscript{81, 82}.

The ultra fine range particles are generated almost exclusively by the conversion of gases to lower volatility vapors, followed by homogeneous nucleation\textsuperscript{4, 83}. These particles may have high concentrations in the polluted urban troposphere, for example, in a winter study of downtown Los Angeles Hughes et al. \textsuperscript{84} found that for particles with a diameter between 0.017 – 0.1 \(\mu\)m that there was an average concentration of about \(10^4\)
cm\(^3\). However, this concentration is still a relatively low mass density, about \(\sim 1 \, \mu g \, m^{-3}\). A person living in this environment will typically inhale about \(10^{11}\) of particles in this size range \(^{84}\). This study highlights one of the current conundrums of urban toxicology: are the toxicological effects associated with aerosols determined more by the number of particles, their total mass, or their composition? The human health implications of aerosols will be addressed in further detail in Section 1.5.

The second way of characterizing particles is by composition. Stratospheric aerosols are predominately inorganic \(^1, 4, 76\) and are largely composed of liquid water and ice, nitric acid – nitrate, sulfuric acid – sulfate. Aerosols based on the aforementioned inorganic compounds form polar stratospheric clouds (PSC). Type I PSCs are composed of particles including liquid phase aqueous solutions of sulfuric and nitric acid, solid nitric acid hydrates, and mixed particles of crystalline sulfuric acid trihydrate and nitric acid hydrates \(^1, 85\). PSCs II form at about \(2 – 5\) K below the ice frost point (188 K) and are mainly ice crystals \(^1, 86\). The chemistry of PSC is important to the legacy of both atmospheric chemistry and the aerosol research community since the photochemistry at the surfaces of particles in these clouds is key in the ozone depletion effect (i.e. the ozone hole effect). In 1985 Farman and coworkers \(^87\) reported massive annual deceases of stratospheric ozone of the Antarctic in the polar spring (September – October). Molina and Molina \(^88\) proposed the following ozone destroying reaction sequence involving gas phase homogeneous photochemistry of ClO:

\[
(1.16) \text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}
\]
(1.17) $\text{Cl}_2\text{O}_2 + h\nu \rightarrow \text{Cl} + \text{Cl} + \text{O}_2$

(1.18) $2[\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2]$

This gives a net reaction of:

(1.19) $2\text{O}_3 + h\nu \rightarrow 3\text{O}_2$.

There was a distinct problem with this model in regards to the ozone depletion condition observed by Farman et al. The highest concentrations of ClO compounds are found at altitudes of 35 – 45 km over Antarctica; while balloon measurements by Hofmann et al. clearly showed that the most significant depletion was occurring at altitudes of 10 – 20 km. There was simply not enough ClO at that altitude to generate the requisite ClO concentration to account for the observed ozone depletion by homogeneous gas phase chemistry alone.

The heterogeneous chemistry at the surface of particulate in PSC plays a critical role in the ozone depletion cycle. These clouds exist at an altitude of 10 – 25 km, which encompasses the strata that the most acute ozone depletion was observed. The most important chlorine liberating step is the heterogeneous reaction that occurs on the surface of particles in PSC:

(1.20) $\text{HCl} \rightarrow \text{HCl (surface)}$

(1.21) $\text{HCl (surface)} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3 (surface)$
(1.22) \( \text{Cl}_2 + h\nu \rightarrow 2 \text{Cl} \)

(1.23) \( 2 [\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2] \)

(1.24) \( \text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M} \)

The net reaction of (1.21) – (1.24) is:

(1.25) \( \text{HCl (surface)} + \text{NO}_2 + 2 \text{O}_3 \rightarrow \text{ClO} + \text{HNO}_3 (\text{surface}) + 2 \text{O}_2 \).

Other reactions involving the heterogeneous chemistry of surface bound HCl and gas phase \( \text{HOCl}^{92, 93} \) and \( \text{N}_2\text{O}_5^{94} \), as well as reactions involving surface water \(^{95} \) with \( \text{ClONO}_2 \) occur on these surfaces and also depletes ozone. It should be noted that these mechanisms indirectly support the earlier proposal by Molina and Molina \(^{88} \) given by Reactions 1.16 – 1.19, by building up a pool of ClO via these surface reactions. The seasonal oscillations in the ozone depletion cycle stem from the concomitant need for cold temperatures (to ensure PSC formation requisite for heterogeneous chemistry) and sunlight required for photochemistry (e.g. Reaction 1.22). Besides the ramifications towards better atmospheric management that stemmed from the theoretical and field studies of the ozone depletion effect, such as controls placed that limit chlorofluorocarbon emissions, the spotlight was thrown upon the potential impact that aerosols have on the global environment.

Inorganic aerosols dominate the chemistry of the stratosphere and are also present in the troposphere. Milford and Davidson \(^{96} \) have an extensive compilation of
data of the composition of tropospheric particles and found that the most common metals and metalloids in the crust (Si, Al, Fe, Ca, Na, K, and Ti) are enriched in the tropospheric aerosols relative to the crust. These enrichments in part may stem from anthropogenic activities. For example calcium has about a 3-fold enrichment in the troposphere and may stem from crushed limestone used in road paving material ⁹⁶. A more significant example is lead, which is enhanced by a factor of about 1500 ⁹⁶ and is strongly correlated with anthropogenic emissions, most notably the combustion of leaded gasoline ⁹⁷.

Inorganic aerosols are also generated over the marine environment via wave action that entrains air, forming bubbles that subsequently rise to the air-sea interface (i.e. the marine microlayer) and burst, ejecting small droplets into the air ⁹⁸, ⁹⁹. These particles nominally have the same concentrations of most elements as seawater, and subsequently are primarily aqueous sodium chloride. However there is an observed enrichment of several metal and metalloid species in the droplet forming process, with perhaps the most notable being boron ¹⁰⁰. Also, while the core of these particles is primarily sodium chloride, the exterior is usually coated with an organic layer ¹⁰¹-¹⁰⁴. This layer is believed to be formed as the bubbles rise and organics adsorb onto the surface as well enrichment that occurs as the bubble bursts through the marine microlayer ¹⁰⁵, ¹⁰⁶. These organics are especially rich in lipids ¹⁰⁶, ¹⁰⁷, including fatty acids and their derivatives such as fatty alcohols. There is expressed concern as of late about the role that these organic coatings have in the heterogeneous chemistry of marine aerosols, including the photochemical generation of the chlorine radical ¹⁰⁸, ¹⁰⁹.
One of the main differences between the particulate matter of the stratosphere and troposphere is that the latter is typically much richer in organic compounds than the former. Typical tropospheric aerosols at mid-latitudes contain between 20 – 50 % organics by mass and are these compounds are found predominately found in fine mode particulate\textsuperscript{40, 41, 110}. Higher mass percentages (up to 90\%) of organic compounds have been reported and appear to correlate with specific biogenic events such as plankton blooms\textsuperscript{111} and are common over tropical forests\textsuperscript{76, 112}. There is a wide variety of chemical classes that have been identified in organic aerosol including alkanes (e.g. \textit{n}-alkanes, steranes) organic acids (e.g. \textit{n}-alkanoic acids, dicarboxylic acids, and polycarboxylic acids), alkanals, aromatic compounds (e.g. polycyclic aromatic hydrocarbons, and polycyclic aromatic ketones), quinines, steroids, and diterpenoid acids\textsuperscript{110, 113, 114}. As noted with marine aerosols\textsuperscript{101-104}, these organic compounds often form coatings and the recent study by Tervahattu et al.\textsuperscript{115} shows evidence that continental sulfate aerosols may be coated as well.

Organic aerosols are often delineated by the way they are emitted into the troposphere. Primary organic aerosols (POAs) are emitted directly into the troposphere as particles with sources including combustion processes (e.g. fossil fuel combustion\textsuperscript{73, 74, 116, 117} and biomass burning\textsuperscript{117, 118}) and the bubble bursting process in the marine microlayer\textsuperscript{101-104}. Secondary organic aerosols (SOAs) are formed in the troposphere by mass transfer to the particulate of low vapor pressure products of the oxidation of volatile organic compounds (VOCs)\textsuperscript{119, 120}, with common oxidants being OH, ozone, NO\textsubscript{3}, and in the marine environment the chlorine radical. VOCs are linked to both anthropogenic\textsuperscript{121},
and biogenic emissions\textsuperscript{121, 123, 124}. While recent assessments indicate that on a global basis VOCs from biogenic sources exceeds anthropogenic emissions there is also great uncertainty in the global estimates of both these sources of SOA\textsuperscript{41, 121}. In the context of SOA formation VOCs are linked into categories of \textit{i}) isoprene, \textit{ii}) terpenes, \textit{iii}) other reactive VOC (ORVOC, atmospheric lifetime $< 1$day), and \textit{iv}) other VOC (OVOC, atmospheric lifetime $> 1$ day), noting that the common volatile organic compound methane is typically abnegated from this classification system and is not considered to be important in SOA formation. The following discussion will place emphasis on isoprene and terpenes, since they probably have a more important role in SOA formation than ORVOC and OVOC with Griffin et al.\textsuperscript{125}, estimating about 30\% of ORVOC and OVOC have the potential to form SOA.

Isoprene ($C_5H_8$) is probably the single most important source of VOCs to the troposphere; accounting for about half of the mass of biogenic VOC\textsuperscript{121, 124}. Isoprene is emitted mainly from vegetation and is estimated to have a global emission range of 250 – 750 Tg C $y^{-1}\textsuperscript{121, 124}$. The oxidation products of isoprene lead to less volatile compounds including glycol aldehyde, hydroxy acetone, and methyltetrols that are common in SOA. These compounds are believed to be common constituents of high molecular weight, water soluble, matter referred to as humic acid like substances (HULIS) that is frequently observed in both hydrometeors\textsuperscript{126-128} and tropospheric aerosols\textsuperscript{127, 129, 130}. The formation and chemical constitution of HULIS, and its role in the atmosphere, especially in the formation of cloud condensation nuclei (CCN) is a topic of current concern and high uncertainty in the atmospheric chemistry research community as of late\textsuperscript{131-133}. 
Terpenes are organic compounds that are derived from isoprene with over 5000 species identified to date as reviewed by Geron and coworkers \textsuperscript{134}. However, the monoterpenes (C\textsubscript{10}H\textsubscript{16}, composed of two isoprenes) alpha-pinene, beta-pinene, sabinene, and limonene are estimated to account for 40 – 80 \% total terpene emissions and from 10 – 50 \% of biogenic VOCs on a global scale\textsuperscript{4,134}. Some of the terpenes have very high potential to form SOA, such as the sesquiterpenes (C\textsubscript{15}H\textsubscript{24}, composed of three isoprenes) that have approximately 100\% potential of forming SOA\textsuperscript{41}.

Before proceeding to more detailed discussion of the oxidative processing of fatty acid aerosols, which is the main subject of the work presented herein, some of the important implications of atmospheric particulate is in order. Emphasis will be placed upon impact of particulate on global climate and human health: two topics that provide motivation for the current research on atmospheric aerosols.

1.4. Aerosols and Climatology

The interaction of particulate matter with radiation is of central interest to the atmospheric research community in this age of major global climate change. Particulate - radiation phenomenology is divided into two main categories: direct and indirect interactions. (A recent class of interactions denoted as semi-direct effects \textsuperscript{135} has appeared in the literature in the last several years. For simplicity, these interactions will be grouped with the indirect aerosol effects.)
1.4.1. Aerosol Direct Effects

The aerosol direct effect refers to the influence that particulate matter has on climate by scattering and absorbing solar radiation. An important parameter that dictates the regime of scattering and absorption of radiation by a particle is given by a dimensionless size parameter ($\alpha$):

$$\alpha = \frac{\pi D_p}{\lambda},$$

where $D_p$ is the particle diameter and $\lambda$ denotes the wavelength of the incident solar radiation. For the purpose of this work we shall only consider key points of the elastic scattering by a spherical particle (i.e. Mie-Debye-Lorenz theory or simply Mie theory $^{136}$).

One of the key results of Mie theory is that the scattering of radiation by a spherical particle can be divided into 3 regimes based on the magnitude of the dimensionless size parameter$^{1,136}$:

- $\alpha \ll 1$, Rayleigh scattering regime: The particle is much smaller than the wavelength of the incident radiation.
- $\alpha \gg 1$, Geometric scattering regime: The particle is much larger than the wavelength of the incident radiation.
- $\alpha = 1$, Mie scattering regime: The particle is of similar size as the wavelength of the incident radiation.
In the following subsection key results on the respective theories of scattering for the upper and lower limiting case regimes will be presented. A discussion of the effects of aerosols on global climate, with emphasis on the role of organic aerosols, will follow this summary.

1.4.1.1. Rayleigh Scattering

Rayleigh scattering becomes important when a particle is much smaller than the wavelength of the incoming radiation\(^1, ^{136}\). Rayleigh scattering is typified by having symmetric intensity of forward and back scattered radiation. It should also be noted that although Mie theory is formally derived for the interactions of spherical particles with radiation, the Rayleigh scattering effect is approximately independent of the shape of the particulate. Before preceding it is useful to present the dimensionless parameter known as the extinction efficiency (\(Q_{\text{ext}}\)):

\[
Q_{\text{ext}} = Q_{\text{scat}} + Q_{\text{abs}}
\]

with \(Q_{\text{scat}}\) denoting the scattering efficiency and \(Q_{\text{abs}}\) being the absorption efficiency. These efficiencies are all functions of \(\alpha\) as well as the (normalized) refractive index of the medium (\(m\)):

\[
m = \frac{N}{N_o},
\]
with $N$ being the complex index of refraction given by a real part ($n$) and an imaginary part ($k$):

$$N = n + ik.$$  

In the context of the scattering of radiation by a particle $N$ is the complex index of refraction for the particle while $N_o$ is the refractive index of the medium i.e. air. Physically the real part and imaginary parts of the index of refraction represents the non-absorbing and absorbing components, respectively. Fundamentally $N_o$ is a complex function as well, but in air $N_o = 1$ (e.g. $N_o = 1.00029 + 0i$ at $\lambda = 589nm$)\(^1\), so this implies in air:

$$m = N = n + ik$$

It can be shown\(^1,136\) that $Q_{abs}$ is directly proportional to $\alpha$ while $Q_{scat}$ is directly proportional to this parameter to the fourth power, and $\alpha \ll 1$ this means that:

$$Q_{abs} \gg Q_{scat}.$$  

Also, the wavelength of the incident radiation, $\lambda$ is inversely proportional to the dimensionless size parameter, $\alpha$ this gives the familiar relationships\(^ {136,137}\)
\[ Q_{\text{scat}} \propto \frac{1}{\lambda^4} \]

\[ Q_{\text{abs}} \propto \frac{1}{\lambda}. \]

The first proportionality results in smaller particles more efficiently scattering shorter wavelengths of incident radiation. Moreover the efficiency of extinction \( Q_{\text{ext}} \) is greater for shorter wavelengths. In the context of radiation in the visible region of the spectrum this effect results in light that is toward the blue being more efficiently extinguished than light that is towards the red region of the visible spectrum. Concisely, an increase in particulate matter results in a red shift in the atmosphere, which is in accord with Lord Rayleigh’s observation: the sky is bluest where the air is the least polluted and purest.

1.4.1.2. Geometric Scattering

Geometric scattering is important when particles are much larger than the incident radiation i.e. \( \alpha \gg 1 \). The scattering behavior by particles in this regime sharply contrasts the case of Rayleigh scattering. Geometric scattering is strongly dependent on the shape of the particle, unlike Rayleigh scattering where it is effectively independent of shape\(^{136}\). Some of the key results for the special case of a spherical particle are presented below. It should be noted that the spherical case is particularly important for atmospheric chemistry and physics since water droplets are the most important class of particles that
satisfy $\alpha \gg 1$. Water also is very weakly absorbing so and is typically considered as non-absorbing$^1$.

The scattering efficiency of a large, non absorbing sphere, such as a water droplet, can be expressed as the sum of the diffraction, reflection, and transmission, respectively:

$$Q_{\text{scat}} = Q_{\text{diff}} + Q_{\text{refl}} + Q_{\text{trans}}.$$ 

Since the extinction efficiency is defined as the sum of scattering and absorption efficiencies and the later is close to zero for a water droplet,

$$Q_{\text{ext}} = Q_{\text{scat}}$$

It has been shown experimentally$^{136}$ that for very large $\alpha$ such as for a water droplet (relative to ultraviolet, visible and infrared radiation) that the extinction efficiency approaches 2:

$$\lim_{\alpha \to \infty} Q_{\text{ext}} \to 2$$

This well-known experimental result is not in accord with geometric optics which predicts that the extinction efficiency approaches unity at this limit$^{137}$. In their treatise on light scattering by particles, Bohren and Huffman$^{136}$ explain this so-called extinction paradox in physical terms, namely that all incident light that is not reflected in a very
large, weakly absorbing sphere, is eventually absorbed, provided that the imaginary term of the refractive index is not exactly zero. Succinctly, even with very small absorption, all the transmitted light will be absorbed in a sufficiently large sphere.

1.4.2. Direct Aerosol Effects and Climate

In this section the relationship between direct aerosol effects and global climate will be discussed. Emphasis will be placed upon comparing what is known about four prevalent classes of aerosols of the lower atmosphere, namely sulfate aerosols, mineral dusts, soot, and organic aerosols. It should be noted that special emphasis will be placed on the last class of particulate, organic aerosols. As shall be explained, far less is known about the aerosol radiative effects (direct and especially indirect aerosol effects) of organic aerosols than the other three classes. As will be introduced in this section, and further elaborated on the section on indirect aerosol effects, this uncertainty arises in part from our current lack of knowledge on how fine and ultra fine organic aerosols age in the lower atmosphere.

1.4.2.1. Direct Aerosol Effects of Sulfate Particulate Matter

Sulfate aerosols are ubiquitous to the lower atmosphere and the majority of studies to date on direct aerosol effects have used this class of particles as a model system\textsuperscript{59, 76, 138-140}. In accord with the commonly used definition, the term ‘sulfate
aerosols” refers to particulate that is predominately sulfate (by mass) including aerosols rich in sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, and NH\textsubscript{4}HSO\textsubscript{4}. The scattering efficiency of sulfate aerosols varies with the relative humidity (RH) since the particles diameter and subsequently its dimensionless size parameter (\(\alpha_{SO^\text{2}-}\))\textsuperscript{1} vary with the hydration of the particles. The size parameter (\(\alpha_{SO^\text{2}-}\)) is usually measured by determining \(\alpha_{SO^\text{2}-}\) at a reference RH (usually 30\%) then multiplying by the ratio of a factor \(f(RH)\) scattering cross sections at the desired RH to the reference RH,\textsuperscript{,}

\[ \alpha_{SO^\text{2}-} = \alpha_{SO^\text{2}-}^{RH} f(RH) \]

Sulfate aerosols that are mainly sulfuric acid are always hydrated under atmospheric conditions. However sulfate aerosols that are primarily composed of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, and/or NH\textsubscript{4}HSO\textsubscript{4} have to reach a threshold RH where the particles spontaneously absorb water and undergo a phase transition from solid to a saturated aqueous solution. The RH at which this transition occurs is called the deliquescence relative humidity (DRH) and as the RH is increased beyond the DRH more water condenses onto the particle and goes into solution, the particles increase in size, and subsequently \(\alpha_{SO^\text{2}-}\) increases. This is an equilibrium process. However this equilibrium process is usually non-reversible, such that starting at a \(RH > DRH\) and decreasing the ambient relative humidity does not generally result in crystallization at the DRH but results in the formation of a (meta-stable) supersaturated solution. The crystallization in
this case will occur at a much lower relative humidity ($RHC$). For (NH$_4$)$_2$SO$_4$ and NH$_4$HSO$_4$ the values of $DRH(RHC)$ at 298 K are 80 $\%^{141, 142}$ (37 $\%^{142}$ and 39 $\%(<5\%)^{142}$ respectively. This hysteresis behavior of (NH$_4$)$_2$SO$_4$ and NH$_4$HSO$_4$ aerosols presents a conundrum to the atmospheric research community and complicates the computational studies of the optical properties of this class of particulate. It is difficult to know whether ambient sulfate aerosol loads have experienced rising or falling $RH$ history which affects how the particle responds to a subsequent change in $RH$ and affects the calculated $f(RH)$ and subsequently $\alpha_{SO_4^{2-}}$. This can be addressed to some extent by detailed source apportionment of the particulate and a detailed record of its transport and meteorological condition to which the aerosol parcel is exposed. Typically for computational studies the two hysteresis curves (i.e. particle size as a function of $RH$) are taken as representations of the extremes of the particles size and intermediary values are incorporated into models$^{143-145}$. The details of the modeling of sulfate aerosol effects on global climate is beyond the scope of this work but interested readers can refer to the extensive body of literature on this topic$^{59, 76, 80, 138, 143-146}$. It should be noted that these estimates typically employ a combination of remote sensing and emissions data with modeling. Further complication arise from the observation that most sulfate aerosol parcels contain two or more of the aforementioned sulfate compounds and are often observed as external or internal mixtures with non-sulfate components, especially soot, as will be discussed in more detail in Section 1.4.2.2. Furthermore, recent studies by Tervahattu and coworkers$^{115}$ showed strong evidence that continental sulfate aerosols are generally covered with thin films of organic matter, especially fatty acids. At the time of
writing there is no extensive work that addresses how these fatty acid films affect the optical properties of sulfate particulate.

Despite the aforementioned complications, there is almost complete consensus that sulfate aerosols contribute to a negative global mean (radiation) forcing i.e. these aerosols contribute towards global cooling by scattering radiation out of the atmosphere. The range of this global mean forcing $\Delta F_{SO_2}$ is from about -0.3 to -1.3 $Wm^{-2}$. These estimates tend to agree that the higher magnitude values of $\Delta F_{SO_2}$ are from box model calculations, as opposed to three-dimensional models. This probably arises from box models abnegating the contribution of the negative forcing from cloud cover that often has spatial-temporal correlation with $SO_2$ emissions and sulfate aerosols.

1.4.2.2. Direct Aerosol Effects of Soot

Carbonaceous particulate matter of the atmosphere can be divided into two main categories: organic aerosols and soot. Soot particulate matter, or simply soot, is composed of elemental or graphitic carbon and in the older literature is often referred to as black carbon. The latter term is a source of some confusion, in that carbon black (c.f. black carbon) is similar to soot except having a much higher surface-to-volume ratio. Soot arises mainly from the incomplete combustion of fuels and very often is found in aerosol parcels with sulfate particles; however, the optical properties of the former particles sharply contrast the latter. Sulfate aerosols scatter radiation and are weakly or
non-absorbing, while conversely soot strongly absorbs radiation as is indicated by the imaginary terms of the indices of refraction for these two classes of particles, using (NH₄)₂SO₄ that is a common form of sulfates found in aerosols¹:

\[ m_{\text{soot}} = 1.90 - 0.66i \ (\lambda = 530\text{nm}) \]

\[ m_{(\text{NH}_4)_2\text{SO}_4} = 1.53 - 0i \ (\lambda = 530\text{nm}). \]

As noted previously, the mixing state of soot and sulfate aerosols presents major corundum in atmospheric chemistry. Since soot and sulfate aerosols often arise from form the same emission source, fossil fuel combustion, they are often observed together in aerosol parcels. In an aerosol parcel soot and sulfate particles can be found in externally mixed aerosols (separate soot and sulfate particles), internally mixed particles, and “core-shell” particles (soot coating, sulfate interior or core), or in a combination of these three regimes as shown in Figure 1-1.
Figural 1-1. Mixing states of soot (black) and sulfate (white) particles.

As summarized by Jacobson $^{58}$, recent studies indicate that the mixing state of these aerosols significantly affect their optical properties and subsequently their radiative forcing. Jacobson has calculated a forcing of $+0.54 \text{ Wm}^{-2}$ for soot-sulfate core-shell particles, $+0.78 \text{ Wm}^{-2}$ for internally mixed particles, and $+0.27 \text{ Wm}^{-2}$ for external mixtures $^{58}$. Recent emphasis$^{57-59, 151}$ has been placed on getting better assessments of the mixing states of soot-sulfate in atmospheric aerosol parcels and applying these results to global models to get more realistic estimates of the forcing from these important classes of particles that are emitted from fossil fuel combustion. The positive forcing of soot may be the second most important contributor to global warming, only exceeded by the effects of CO$_2$ ($+1.56 \text{ Wm}^{-2}$) $^{59, 152}$. Although controversial, the recent work by Andreae $^{59}$ indicates that the positive forcing of soot exceeds the magnitude of the negative forcing of sulfate aerosols and suggests that the overall forcing of aerosols may be positive. This second point is contested in part on the basis that there is a very limited amount of
information on the direct and indirect radiative forcing of another common class of atmospheric particulate matter: organic aerosols, which are the topics of Sections 1.4.2.4 and 1.4.3, respectively.

1.4.2.3. Direct Aerosol Effects of Mineral Particulate

Minerals are the most common constituent of ubiquitous atmospheric dusts and are predominately found in the coarse mode $^{43,96}$. Most of the metals in these dusts are present as oxides with some prevalent compounds being $\text{Al}_2\text{O}_3$, $\text{CaO}$, $\text{Fe}_2\text{O}_3$, $\text{SiO}_2$, and $\text{Na}_2\text{O}^{44}$. These dusts are formed mainly by frictional forces, and as noted earlier, episodic natural events, such as sandstorms, contribute a significant mass fraction of mineral dusts to the atmosphere. However, according to estimates by Tegen et al. $^{153}$, recent anthropogenic activities (e.g. agriculture) have approximately doubled the rate of emissions of mineral dusts ($\leq 20 \ \mu\text{m}$) with total global source strength of $\sim 2000 \text{ Mt y}^{-1}$. Mineral dusts generally both scatter and weakly absorb solar radiation, having a non-zero imaginary term in their refractive index, e.g. $^{153}$:

$$m_{\text{dust}} = 1.56 + 0.006i \quad (\lambda = 550 \text{ nm}).$$

The imaginary term in the index of refraction for mineral dust is strongly dependent on the wavelength of the incident radiation. These dusts absorb more strongly for thermal wavelengths (i.e. infrared radiation) than shorter wavelengths, and this
contributes towards positive forcing (this is referred to as thermal forcing). Recent studies by Balkanski et al. 44 suggest that the forcing by dusts strongly depends on the brightness of the underlying surface. Over bare surfaces that have large surface albedo (i.e. bright, reflective surfaces), such as the desert, mineral dusts tend to warm the atmospheric column. Conversely, over dark surfaces (i.e. low surface albedo) such as oceans and deciduous forests, mineral dusts tend to cool the atmospheric column. Physically these radiative affects arise from high surface albedo (bright) regions reflecting most solar radiation back towards the top of the atmosphere then scattered in part back towards Earth’s surface by mineral dust. Conversely, low surface albedo (dark) regions strongly absorb solar radiation such that the cooling effects of mineral dust come mainly from the absorption of thermal radiation. The evaluation by Balkanski et al. 44 suggests that the overall forcing of mineral dusts cools the Earth-atmosphere system, with the total top-of-the-atmosphere forcing from mineral dust between -0.03 and -0.25 Wm\(^{-2}\). This contrasts the earlier evaluation by the International Panel of Climate Change (IPCC) 154 of -0.6 to +0.4 W m\(^{-2}\). While the details of all the considerations that were the basis of these important results is beyond the scope of this introductory discussion, it should be noted that the main apparent advantage of the very recent estimates by Balkanski et al. 44 (c.f. the IPCC 154) is the incorporation of more accurate indexes of refractions for the main components of mineral dusts 155 such as the iron oxides. In summary, ubiquitous mineral dusts scatter and absorb radiation and there is still active debate on whether they contribute to positive or negative radiative forcing. This presents further challenges for
estimating the effects of anthropogenic and naturally occurring particles on global climate.

1.4.2.4. Direct Aerosol Effects of Organic Aerosols

Arguably, organic aerosols have the greatest uncertainty in their direct aerosol effects of the main classes of particulate found in the lower atmosphere (c.f. sulfate, soot, and mineral particulate matter). Unlike the case of sulfate aerosols, the deliquescence properties of organic aerosols are not well established \(^1\). (Recall that the deliquescence properties affect the size parameter (\(\alpha\)) and subsequently optical properties of the particulate.) The deliquescence properties of organic aerosols are not only important for the direct aerosol effects but also important for the indirect aerosol effects, discussed in Section 1.4.3. Organic aerosol parcels typically contain hundreds to thousands of unique compounds \(^{41, 110, 113, 156}\). In the recent evaluation by Kanakidou et al. \(^{41}\) on the uncertainties of the impact of organic aerosols on global climate the following questions were presented that need to be more accurately addressed to facilitate better assessments of the role of organic aerosols on modifying global climate:

— What are mechanisms of secondary organic aerosol (SOA) formation and how much SOA is formed in the lower atmosphere?

— What is the role of nucleation of organic aerosols on a global scale?
— What are the important mixing states of organic aerosols? What affects do these mixing states have on the optical properties of organic aerosols?

— How do organic aerosols age (by oxidation and photochemistry) in the lower atmosphere?

— How do semivolatile organic components partition between the gas phase and particles?

A better understanding of these compositional and thermo-chemical considerations will ultimately allow for a more realistic assessment of the optical properties of organic aerosols and their impact on global climate. The results presented in this dissertation address some of these uncertainties by giving a better depiction of the oxidative processing of a ubiquitous class of organics found in the troposphere, fatty acids, using oleic acid as a model compound.

The majority of global models of direct radiative forcing incorporate the following aerosol optical properties: the extinction coefficient, single scattering albedo, and asymmetry factors, which are calculated from Mie theory and require wavelength and size dependent refractive indices for the particles. As reviewed by Kanakidou et al., until recently almost all of the global models that incorporated organic aerosols into their computations have assumed that the multicomponent organic particles were internally well-mixed and have employed a constant extinction coefficient for the organic particles. The incorporation of organic aerosols into global three dimensional models by Lioussse et al. gave precedent to this approximation. In that study Lioussse et al. assumed a constant extinction coefficient for the three wavelength bands considered, and
applied the values for soot to organic aerosols. Furthermore, to account for the effects of RH on particle size and subsequently on the optical properties they treated organic aerosols like sulfate particles.

Since the nascent study by Liousse et al. only a relatively small fraction of the global climatic models that have incorporated the direct aerosol effects have included organic aerosols into the model formulation and very few have considered the role secondary organic aerosols. In terms of the properties that relate to organic aerosols, most of these models treat the extinction coefficient as a single value at a given wavelength. However, as summarized by Kanakidou et al. the adopted values of these extinction coefficients vary by a factor of about 3–4. Another requisite property for these models is the single scattering albedo (ω) that is the ratio of the scattering and extinction efficiencies, or equivalently, the ratio of the ratio of the scattering and extinction cross sections (i.e. $C_{\text{scat}}$ and $C_{\text{ext}}$ respectively):

$$\omega = \frac{Q_{\text{scat}}}{Q_{\text{ext}}} = \frac{C_{\text{scat}}}{C_{\text{ext}}}.$$ 

Most global models assume that organic aerosols are weakly absorbing such that ω is slightly less than unity i.e. $\omega \sim 0.94–0.98$, and a few models have treated organic aerosols as purely scattering (i.e. $Q_{\text{scat}} = Q_{\text{ext}}$ and $\omega = 1$). As of late, most models treat the single scattering albedo as independent of wavelength and estimate ω using effective particle radii. As addressed by Kanakidou et al., the use of effective
particle radii highlights the need to develop a better understanding of how aerosol growth responds to $RH$ that subsequently requires a better understanding of the composition and atmospheric aging of organic aerosols, which is the motivation of the research presented in this dissertation.

As of late, there is general agreement that organic aerosols have a negative forcing from the direct aerosol effects. For example, Chung and Seinfeld\textsuperscript{158} have one of the few models that incorporated the effects of SOA and calculated that the direct aerosol effects from organic aerosols had a direct forcing of -0.09 Wm\textsuperscript{-2}. To put this in the context of overall direct forcing by all aerosols, a recent estimate\textsuperscript{160} based on satellite measurements (MODIS) and detailed records of surface wind speed report an annual average global direct radiative forcing of $-1.9 \pm 0.3$ W m\textsuperscript{-2}, but other global models range from $\sim -0.5$ to $-0.9$ Wm\textsuperscript{-2}\textsuperscript{276,140,161}. Though beyond the scope of this introduction, it should be noted that the wide discrepancy of estimates of overall direct forcing (and subsequently the relative contribution of organic aerosols) stem mainly from: variations in estimates in surface albedo over land and oceans; variations in estimating optical depth; differences in global aerosol inventories based on sampling bias; and the mixing state of aerosols. Interested readers should refer to recent assessments by the AeroCom\textsuperscript{162,163} project that diagnoses the sources of discrepancy between these climate models for further details.

1.4.3. Indirect Aerosol Effects and Climate
Atmospheric particles can affect the climatic system by changing the physical properties of clouds. The mechanisms by which these changes occur are called indirect aerosol effects. The indirect aerosol effects mainly originate from particles acting as cloud condensation nuclei (CCN) or as ice nuclei (IN); and particles suppressing atmospheric convection, i.e. the semi-direct effect. The two most frequently discussed specific indirect aerosol effects, the Twomey and cloud lifetime effects will be discussed first in the context of atmospheric particles acting as CCN, with emphasis on the former effect (see Section 1.4.3.1). Other indirect aerosol effects for which there is very little forcing data on are summarized in Table 1-1 that is adapted from the recent review by Lohmann and Feichter.  

<table>
<thead>
<tr>
<th>Effect</th>
<th>Cloud type</th>
<th>Key points</th>
<th>F (Wm$^{-2}$) (Top of atmosphere)</th>
<th>F (Wm$^{-2}$) (Earth’s surface)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Twomey or cloud albedo effect</td>
<td>All clouds</td>
<td>More numerous smaller cloud particles reflect more solar radiation</td>
<td>-0.5 to -1.9</td>
<td>-0.5 to -1.9</td>
</tr>
<tr>
<td>Cloud lifetime effect</td>
<td>All clouds</td>
<td>Smaller cloud particles decrease ppt efficiency increasing cloud lifetime</td>
<td>-0.3 to -1.4</td>
<td>-0.3 to -1.4</td>
</tr>
<tr>
<td>Thermodynamic effect</td>
<td>Mixed phase clouds</td>
<td>Smaller cloud droplets delay onset of freezing</td>
<td>unknown</td>
<td>unknown</td>
</tr>
<tr>
<td>Glaciation effect</td>
<td>Mixed phase clouds</td>
<td>More ice nuclei increase ppt efficiency decreasing cloud lifetime</td>
<td>unknown</td>
<td>unknown</td>
</tr>
<tr>
<td>Riming effect</td>
<td>Mixed phase clouds</td>
<td>Smaller droplets decrease efficiency of contact freezing between colliding ice and super-cooled droplets</td>
<td>unknown</td>
<td>unknown</td>
</tr>
<tr>
<td>Surface energy budget effect</td>
<td>All clouds</td>
<td>Increased aerosol and cloud optical thickness both decrease the net surface solar radiation</td>
<td>n/a</td>
<td>-1.8 to -4</td>
</tr>
<tr>
<td>Semi-direct effect</td>
<td>All clouds</td>
<td>Particles absorb solar radiation, promotes cloud evaporation</td>
<td>+0.1 to -0.5</td>
<td>Probably larger that F at top of atmosphere</td>
</tr>
</tbody>
</table>

Table 1-1. Indirect aerosol effects and estimates of forcing.
1.4.3.1. Twomey and Cloud Lifetime Aerosol Indirect Effects

Clouds form by the cooling of an air parcel to a temperature at which the supersaturation of water vapor can occur. At supersaturation the aerosols within a cloud can act as cloud condensation nuclei (i.e. the aerosol particles are said to be “activated”) and form cloud droplets. These droplets grow in size as they take up additional water vapor. The diameter the aerosols become activated is a function of its water soluble material content \(^{41, 110, 120, 127, 128, 130, 132}\). Anthropogenic emissions can dramatically affect the aerosol number concentrations in a polluted troposphere and act as a perturbation to the cloud formation process \(^{165, 166}\) and as will be discussed, modify the optical properties of the cloud. Anthropogenic aerosol emissions can have a pronounced effect on cloud formation, for example, Twomey et al. \(^{165}\) reported an increase of the CCN concentrations from ~50 cm\(^{-3}\) to ~4500 cm\(^{-3}\) as a clean air parcel passed from a pristine marine environment to an industrialized region of Australia.

Clouds that form in regions of high particulate content typically have smaller and higher concentrations of droplets. The Twomey or cloud albedo effect is an enhancement of the reflectivity of a cloud due to more but smaller cloud droplets in a cloud of constant liquid water content water \(^{167}\). This arises from an increase in the number of light scattering events within the cloud which increases both its optical depth and its albedo or reflectivity. The optical depth of a cloud \((\tau_c)\) with a depth \((h)\) is given by Beer-Lambert’s law:
\[ \tau_c = b_{ex}(\lambda)h \]

It can readily be shown that for a cloud with a monodisperse distribution of droplets \(^1\):

\[ \tau_c \propto hL^{2/3}N^{1/3} \]

where \( L \) is the liquid water content (i.e. mass of liquid water per unit volume of air), and \( N \) is the number concentration of the droplets; such that the optical depth of the cloud goes as the number concentration of droplets to the one-thirds power.

The relationships shown in the literature that address the indirect aerosol effects \(^1, 76, 156, 161\) between the cloud albedo (reflectivity) and the optical depth are typically parameterized. This parameterization is typically employed to account for the asymmetry of the light scattered of the particle (i.e. water droplet) and depends on such factors as the homogeneity of the cloud, and droplet size \(^168\). In brief, the asymmetry parameter (\( g \)) is defined as the intensity-weighted average of the cosine of the scattering angle, with readers directed to the work for Lacis and Hansen for further details\(^168\). The two-stream approximation \(^168\) relates cloud albedo (\( R_c \)) to optical depth for non-absorbing, homogeneous clouds:

\[ R_c = \frac{\sqrt{3}(1-g)\tau_c}{2 + \sqrt{3}(1-g)\tau_c}. \]
Hansen and Pollack 169 showed that for typical size cloud droplets ($D_{\text{droplet}} \sim 5-10 \mu m$) that for visible to near-infrared light that $g \approx 0.85$, which upon substitution to the above expression gives:

$$R_c = \frac{\tau_c}{\tau_c + 7.7}.$$

When the optical depth of the cloud approaches zero the cloud albedo approaches zero, while for clouds with a large optical depth (i.e. $\tau_c \gg 7.7$) $R_c \rightarrow 1$, which is common for with clouds with a large number of droplets.

Anthropogenic emissions can dramatically increase the aerosol load in a polluted industrial region and increase the number of droplets in clouds 165, 166 by acting as CCN. One of the main challenges of cloud chemistry and physics is trying to relate the number of particles in a cloud with the concentration of CCN, which is at the heart of the indirect aerosol effects. Fundamentally the CCN concentration is a function of supersaturation ($s$) of the particles and for a (realistic) aerosol parcel that has a size dependent chemical composition and different compositions having different supersaturations and is defined by the relationship 1:

$$CCN(s) = \int_0^\infty f_s(D_p)n(D_p)dD_p,$$
where $f_a(D_p)$ denotes the fraction of particles that are activated at a percent supersaturation at a given diameter ($D_p$), and $n(D_p)$ is the number distribution of the particle population. The prior definition for CCN concentration is rarely used in practice because of the difficulties in making accurate field measurements of the aerosol size composition distribution, and subsequently determining $f_a(D_p)$. Because of these difficulties the CCN concentration is usually calculated as a power series $^{1,173-175}$ with the most commonly encountered form being:

$$CCN(s) = cs^k$$

where $c$ and $k$ are empirical parameters with tabulated values derived from field measurements available in the literature$^{1,174}$.

As of late, there is no fundamental relationship that connects the number density or related property of a particular class of aerosol with the CCN concentration. With sulfate aerosols there is a well-established empirical relationship between cloud droplet number condensations (CDNC) $^{1,176,177}$:

$$CDNC = 10^{2.21+0.41\log(m_{SO4})}$$

where $m_{SO4}$ denotes the mass of sulfate per unit volume of cloud (i.e. $\mu g(SO_4^{2-})m^{-3}$ in this form of the equation). It should be noted that the CDNC increases linearly at low
concentrations of CCN, but behaves nonlinearly for higher CCN concentrations (e.g. transitions occur between linear and nonlinear regimes ~ 600 – 800 cm\(^{-3}\) in continental stratiform clouds \(^1, 178\)). It should be noted that at the time of writing no analogous empirical relationships between the CDNC or CCN and organic aerosol mass or number concentration or similar metric.

The Twomey or cloud albedo effect has a causal relationship to the cloud lifetime (indirect) aerosol effect. As the number of aerosol particles in a cloud with constant liquid water content increases the CCN concentration and CDNC increase, and there is a decrease in droplet size \(^179\). This tends to decrease the precipitation efficiency \(^161\), increase the liquid water content of the cloud \(^161\), increase the cloud thickness \(^180\), and leads to an increase in the cloud lifetime \(^179, 181\). As noted in the review by Haywood and Boucher \(^161\) on the radiative forcing by clouds; the cloud albedo effect of aerosols has received a lot more attention than the cloud lifetime aerosol affect and there is an expressed low levels of confidence \(^154, 161\) in the estimates of the indirect aerosol effects.

1.5. Impact of Aerosols on Human Health

There is an established association between particulate matter concentration and human mortality and morbidity levels \(^182, 183\), especially in polluted urban environments. For example, in an epidemiological assessment of the 20 largest cities and metropolitan areas in the United States Samet et al. \(^184\) found consistent evidence that the concentrations of particles with diameters of less than 10 \(\mu m\) (commonly denoted PM\(_{10}\)
is associated with the rate of death from all cardiovascular and respiratory diseases. The diameter of particulate matter is a key physicochemical parameter in determining biological activity with smaller particles having greater specific surface areas, inferring greater biological activity per unit mass compared to larger particles with similar chemical composition \(^{185}\). The size of the particulate matter is also important in determining where it is deposited in the respiratory system. Coarse particulate matter shows greater fractional deposition in the extrathoracic and upper tracheobronchial regions, while conversely fine particulate matter typically shows greater deposition in deep lung tissue \(^{183}\). There is growing concern about human health effects of even smaller sized particles, namely ultra fine particulate matter. Recent studies \(^{83, 186, 187}\) have shown that while ultra fine particles typically make up very small fraction of the total mass concentration of the aerosol load, in polluted urban environments the number size distribution is dominated by ultra fine particulate, and strongly linked to motor vehicle emissions \(^{83, 186, 188}\) especially from diesel emissions \(^{186, 189}\). As recently summarized by Oberdörster et al. \(^{185}\) ultra fine particles are readily taken up by cells, and can be transported via transeptosis across endothelial and epithelial cells to target sites including the heart and other organs, and can access the central nervous system and ganglia via axonal translocation.

**1.6. Fatty Acid Aerosols**
As of late the atmospheric research community has been giving increasing attention to the role of organic aerosols in the troposphere. This concern has initiated a number of recent reviews focusing on organic aerosols and addressing topics including: laboratory methodology, the oxidative and photochemical aging of organic aerosols; the role of organic acids in forming CCN; the role of bio-aerosols in forming CCN; the role of OA in global climate modeling; humic-like substances (HULIS); the significance of organic films at the air-aqueous interface; as well as comprehensive works that span many of these disciplines. A common theme that echoes throughout many of these works is the importance of developing a better understanding of oxidative processing of OA and its implications to the troposphere.

It is clear that our understanding of the role of oxidative processing of organic aerosols is in its nascent stage. While typical organic aerosols in the troposphere have hundreds to thousands of unique chemical components, we need to develop simple model systems to distill key features of oxidative processing of atmospheric organic aerosol. In this dissertation I present experimental results for an emerging model reaction system, the oleic acid – ozone heterogeneous reaction system (oleic acid is cis-9-octadecenoic acid) that has become the benchmark for future experiments. As shall be discussed below, oleic acid is a monounsaturated fatty acid found in tropospheric aerosols and is employed as a tracer for cooking aerosols.

1.6.1. Sources of Fatty Acid Aerosols and Their Role as Surfactants
Organic acids are ubiquitous in the troposphere and fatty acids make up a significant contribution to this fraction \(^{113,199-201}\). Fatty acids have both anthropogenic and biogenic sources, which will be described in this section and is followed by an account of the role of fatty acids to act as organic surfactants in the troposphere.

Marine aerosols contribute significantly to the global organic aerosol load. Photosynthesis by marine organisms, especially autotrophic organisms such as phytoplankton, produces about 30-60 Pg of organic carbon annually \(^{202,203}\) including lipids. Typical total fatty acid concentrations (dissolved plus particulate) in seawater range from \(~ 3-200 \ \mu g \ l^{-1}\) \(^{107}\). Fatty acids, along with \(n\)-alkanes and total hydrocarbons, are typically enriched on the marine microlayer (i.e. the air–sea interface) compared to the subsurface; for example, Marty et al. \(^{107}\) determined an enrichment of these chemical classes in the microlayer by a factor of 2–5 in the northeastern Atlantic. The similarities between the ratios of the quantities of fatty acids in the marine microlayer and in marine aerosols have long been noted \(^{204,205}\). These surface active agents are ejected into the marine troposphere by a bubble bursting mechanism \(^{204,205,98,99,106}\), with estimates of up to 200 Tg C yr\(^{-1}\) of hydrocarbons available for incorporation into marine organic aerosols proposed \(^{206}\). Organic compounds comprise a significant fraction of the mass of marine aerosols, with estimates between \(~10–50\%\) (wt/wt %) \(^{207,208}\) and elevated concentrations of organic matter on particles may correspond with times of high biological activity \(^{209}\), notably plankton blooms \(^{111}\).

In the marine troposphere, fatty acids with 12-19 carbons (i.e. C12-C19 fatty acids) are commonly observed, with the saturated FA being dominant \(^{107,205,209,210}\). They
make a significant contribution to the organic coatings of sea salt particles. Unsaturated fatty acids, including oleic acid, are also commonly observed, and usually are found at lower concentrations than saturated fatty acids. The detection of unsaturated fatty acids in marine aerosols has been suggested to be indicative of recent biological activity, since unsaturated fatty acids can be oxidized more readily than saturated fatty acids in the atmosphere. For example, Kawamura and Gagosian sampled remote marine aerosols on Enewetak Atoll 1 (Marshall Islands) and found stearic acid was 0.083 ng m⁻³, while the monounsaturated C18 (i.e., oleic acid) was below the limit of detection. Similarly, in the North Pacific Ocean, stearic acid was detected at 0.21 ng m⁻³, while its monounsaturated analogue (i.e. oleic acid) was 0.043 ng m⁻³ with other remote locations and fatty acid concentrations detailed in Table 1 of the report by Kawamura and Gagosian. Similar trends were observed with the C16 saturated and monounsaturated fatty acids (c.f. palmitic and palmitoleic acid). Mochida et al. have also noted the lower abundance of unsaturated fatty acids compared to saturated fatty acids in aerosols in the marine boundary layer of the North Pacific. This study detected fatty acids (C14–C32) and showed a positive correlation between C14-C19 fatty acids with sea salt and biological activity. In this study, it was estimated that between 0.3–14% surface coverage for sea salt aerosols was due to C14-C19 saturated fatty acids.

In rural and remote continental locations, direct forest emissions, especially from vascular plants, are a significant biogenic source of fatty acids including unsaturated fatty acids. The unsaturated fatty acids in these aerosols are often observed to be at lower concentrations than their saturated analogues due to oxidation. For
example, in Harmattan trade wind aerosols of Nigeria, the ratio of saturated to unsaturated C18 fatty acids generally favored the saturated species by factors of 0.6 – 230. Similarly, this ratio was determined to be in the range 1.4 – 56 in aerosols in the western U.S.A. Again, the presence of unsaturated fatty acids in the aerosols was considered to have been an indicator of recent biogenesis.

There is a growing appreciation to the contribution bacteria, pollen, fungi, and other microbial emissions from the biosphere make on the primary biogenic aerosol load, with these sources being rich in membrane lipids including fatty acids. These primary biogenic emissions may have roles in acting as CCN.

Gas and diesel powered vehicles contribute significant amounts of organics to the urban particulate load. Rogge et al. have shown that internal combustion engines that burn gasoline and diesel contribute over 21% of the primary fine particulate organic carbon in Los Angeles. Similarly, Fraser et al. have shown that up to 19.1% of fine particulate organic material can be traced to motor vehicles during the morning traffic peak in Los Angeles. This fine particulate typically contains more than 100 organic components and n-alkanoic acids, including saturated fatty acids make up a considerable fraction of the total organic mass. Rogge et al. found that for non-catalyst automobiles that the main portion of the identifiable organic mass (61.2%) was polyaromatic hydrocarbons (including oxy–polyaromatic hydrocarbon classes); however, in contrast, in catalyst-equipped automobiles n-alkanoic acids, including saturated fatty acids were the major component (53.4%). In catalyst-equipped automobiles, palmitic
acid was the most prevalent of the fatty acid emissions, with an emission rate of 63.9 μg/km\(^2\)\(^2\)\(^1\). Of unsaturated fatty acids, oleic acid was the most prevalent with an emission rate of 5.0 μg/km in the catalyst-equipped automobiles\(^2\)\(^2\)\(^1\).

Cooking emissions are established as an important anthropogenic source of fatty acids in urban environments\(^1\)\(^9\),\(^8\),\(^2\)\(^2\)\(^8\)-\(^2\)\(^3\)\(^0\). Very recently, a series of reports from China\(^1\)\(^1\)\(^6\),\(^2\)\(^2\)\(^5\),\(^2\)\(^6\),\(^2\)\(^3\)\(^1\)-\(^2\)\(^3\)\(^4\) and Hong Kong\(^2\)\(^2\)\(^3\),\(^2\)\(^3\)\(^5\) have indicated that Chinese-style cooking can lead to significant fatty acid emissions. Wang et al.\(^2\)\(^3\)\(^3\) studied organic aerosols in 14 coastal and inland mega-cities in China during the winter and summer 2003. The levels of fatty acids were very high, having an annual average of 769 ng m\(^-3\). Unsaturated fatty acids (e.g. oleic acid and palmitoleic acid) were found in all samples and had an annual total average concentration of 93.6 ng m\(^-3\). The concentration ratios of unsaturated fatty acids compared to saturated FA (e.g. stearic and palmitic acid) were 1.14 ± 0.98 in winter versus 0.43 ± 0.09 in summer, suggesting an enhanced photochemical degradation of the unsaturated fatty acids during the summer\(^2\)\(^1\)\(^2\),\(^2\)\(^3\)\(^3\). The high levels of fatty acids in Chinese cities have been noted by others. Huang et al.\(^2\)\(^2\)\(^5\) reported a seasonal average concentration of fatty acids at 260 – 483 ng m\(^-3\) in particles under 2.5 μm in diameter (these particles are commonly called PM\(_{2.5}\)) in Beijing, with unsaturated fatty acids being present but at lower concentration than saturated fatty acids. Zhao et al.\(^2\)\(^3\)\(^4\) studied four Chinese cooking styles in Guangzhou and determined that fatty acids composed about 73 – 85% of the quantified particulate organic matter in PM\(_{2.5}\). This is similar to an earlier study on emissions of fine particulate from Chinese cooking in Shenzhen by He et al.\(^2\)\(^3\)\(^2\) that reported fatty acids at over 90 % in the quantified organic mass. In a study by Zheng
et al. of solvent extractable organic compounds in PM$_{2.5}$ of ambient aerosols in Hong Kong, fatty acids were the major component at 46 – 80% by weight. It should be noted that these authors considered the role of microbial and vascular plant emissions as well as cooking emissions. A study in Mong Kok, Hong Kong by Sin et al. determined oleic acid to be the predominant fatty acids at ~ 180 ng m$^{-3}$ (my estimate from Figure 5 in their work) and attributed this to evaporation of cooking oils from the many “snack-bars/snack-counters” in that region that deep and stir fry foods in open kitchens in Mong Kok.

As noted previously, organics have been observed as coatings on sea salt particles and there is recent, direct evidence that fatty acids may be a common coating on continental sulfate aerosols. These observations are helping to elucidate the importance of fatty acids as organic surfactants in the troposphere. In prior works, organic surfactants had been hypothesized to reside on atmospheric particulate and the transformation of these surfactants by oxidative processing had been suggested. Ellison et al. proposed a chemical model for the structure, composition and processing of organic particulate. Their model described organic aerosol in the form of an inverted micelle with an aqueous core and an organic surfactant coating, the latter being of biological origin. This model was important in that it suggested that the organic layer was transformed from an inert, hydrophobic film to a reactive, optically active hydrophilic layer via oxidation by atmospheric radicals. Subsequent studies have shown that these organic films are susceptible to oxidation by common tropospheric oxidants, with the oxidized films typically showing considerable change in composition and increased
hydrophilicity. Further details on how organic films at the air-aqueous boundary influence atmospheric processes are given in the recent review by Donaldson and Vaida.

1.7. Ozonolysis

The work presented within the body of this dissertation deals with the oxidation of aerosols containing fatty acid or fatty acid derived compounds (e.g. methyl esters) by ozone. In light of this a summary of ozonolysis of unsaturated compounds is presented.

A simplified version of the ozonolysis of an unsaturated compound in solution is often described by the following three step mechanism (see Scheme 2-1 in Chapter 2 for an example):

- **Step 1)** formation of a primary ozonide
- **Step 2)** decomposition of the primary ozonides to aldehydes (or ketones) and carbonyl oxides (commonly referred to as Criegee intermediates)
- **Step 3)** recombination of the carbonyl oxide and the aldehyde (or ketone) to form secondary ozonides

In the ozonolysis of unsaturated species in solution, particularly at low temperature, secondary ozonides are often observed and have been isolated in high yield.

The reactivity of Criegee intermediates is of central importance in understanding the heterogeneous oxidative processing of oleic acid and similar unsaturated species by ozone. Section 1.7.1 is dedicated to describing the key features of
the electronic structure of Criegee intermediates, which antecedes a discussion on the reactivity of these intermediates in the gas and liquid phases given in Section 1.7.2.

1.7.1. Electronic Structure of Criegee Intermediates

Criegee intermediates are depicted as both zwitterions and biradicals (a.k.a. diradicals) in the literature on the heterogeneous ozonolysis of oleic acid. The discord in this description has its roots in part in the debate on the electronic structure of these intermediates that are extant in the organic chemistry literature\textsuperscript{242,246,247}. Criegee showed that for ozonolysis in solutions there was evidence indicating Criegee intermediates were zwitterionic based on reactivity trends\textsuperscript{241}. On the other hand, as presented in a review by Bunnelle\textsuperscript{246}, other researchers gave computational evidence that these intermediates were singlet biradicals\textsuperscript{248,249}. Revised considerations of some early calculations\textsuperscript{242,249} indicated that the energy difference between the biradical and zwitterionic forms of the smallest Criegee intermediates were artificially large. Most subsequent computational studies focused on simple Criegee intermediates. Semiempirical calculations have been employed to investigate the effects of larger substituents on the electronic structure of Criegee intermediates and mostly indicate that these intermediates have significant biradical character\textsuperscript{246}. The distilling conclusion of these investigations is that the Criegee intermediate electronic structure is best represented as a resonance between the biradical and the zwitterion.
More recent investigations have focused on substituted Criegee intermediates in solution. Density functional theory calculations indicate that the dipolar character is enhanced by progressive methylation. Solvent effects and resonance have also been considered and it has been indicated that zwitterionic character was enhanced with increasing dielectric constant of the solution.

In summary:

- Criegee intermediates most likely have zwitterionic and biradical resonances
- Computational work to date has primarily focused on smaller Criegee intermediates, especially CH$_2$OO
- We do not have an accurate description of the electronic state of Criegee intermediates generated in the ozonolysis of oleic acid, let alone mixed organic aerosols. The electronic state of Criegee intermediates affects reactivity trends; hence the predictions of product formation from ozonized organic aerosols will largely rely on empirical observations.

1.7.2. Gas- and Liquid-phase Reactivity of Criegee Intermediates

In regards to the fate of Criegee intermediates in the oleic acid–ozone heterogeneous reaction system there has been a question as to whether they react in a manner similar to what is observed in ozonolysis in the gas-phase or that in solution. In this section we will present a concise summary of the established reactivity of these intermediates for these cases and in the conclusion of this work sections provide
discussion that the Criegee intermediates react more in accord with solution chemistry. We will not present any details regarding a third experimental regime, namely investigations of Criegee intermediates in inert matrices under cryogenic conditions but interested readers can find several reviews\textsuperscript{246, 247} that cover this topic of extensive research.

As noted by Neeb et al.\textsuperscript{252} regarding the differences in gas-phase and liquid-phase ozonolysis of ethene: “While the formation of the secondary ozonide is the most important reaction of the Criegee intermediate in the liquid-phase, its reaction pathways are quite different in the gas-phase, due to the generally much lower concentrations employed and the absence of solvent molecules.” This statement is applicable towards the ozonolysis of most unsaturated compounds. A significant fraction of gas-phase Criegee intermediates undergo unimolecular decomposition and these channels have been established for the simplest Criegee intermediate, CH$_2$OO\textsuperscript{253-255}. These products include OH and other free-radicals\textsuperscript{252, 256-263}.

As summarized by Neeb\textsuperscript{252}, in the gas-phase Criegee intermediate can undergo collisional stabilization and then can react with a variety of other species including aldehydes, SO$_2$, CO, water NO, and NO$_2$ as well as hydroxyl containing compounds (e.g. alcohols, organic acids)\textsuperscript{264, 265}.

In the gas-phase, Criegee intermediates can undergo spontaneous isomerization to a dioxirane, which by a 1, 2-hydrogen shift isomerizes to an acid (see review by Bunnelle\textsuperscript{246}). This acid is formed in a high energy state and may undergo dissociation if not quenched\textsuperscript{246, 255}. Numerous calculations summarized by Bunnelle\textsuperscript{246} indicate there is
a considerable activation energy barrier between a thermally equilibrated Criegee intermediate and the dioxirane. For the channel of isomerization by the Criegee intermediate to the dioxirane to compete successfully against bimolecular channels the Criegee intermediate must be in a vibrationally excited state. As stated by Bunnelle 246: “Depending on the excess energy between products, and further on the efficiency of collisional deactivation, the carbonyl oxides (i.e. Criegee intermediates) can be formed with sufficient internal energy to isomerize (to the dioxirane) spontaneously.” These discussions focus, for the most, on small Criegee intermediates, most notably, CH$_2$OO. Other fates of these intermediates, such as ejection of atomic oxygen are considered by Bunnelle 246.

The fate of Criegee intermediates in solutions is often quite different than in the gas-phase. As summarized by Bailey 266 these intermediates have the following possible fates in solution:

a) The Criegee intermediate can undergo 1,3-dipolar cycloaddition with the carbonyl containing product that was formed from the decomposition of the primary ozonide. The products of these reactions are secondary ozonides and polymeric ozonides

b) The Criegee intermediate can undergo 1,3-dipolar cycloaddition with other Criegee intermediates to form geminal diperoxides or polymeric peroxides

c) The Criegee intermediate can undergo rearrangement

d) The Criegee intermediates can react with protic solvents (e.g. alcohols, water, acids) and form hydroperoxides
While secondary ozonides are often described as the major products of ozonolysis, there are some important exceptions. One of the most notable exceptions for this discussion is case (d) listed above; namely when the solvent is protic. In that case the Criegee intermediate may react with the protic species as or more efficiently than undergoing 1, 3-dipolar cycloaddition with the carbonyl containing product formed from the decomposition of the primary ozonide \(^{244, 266}\). This route may tend to favor hydroperoxide products \(^{244, 266}\).

As will be discussed, the results of these investigations on the oleic acid–ozone heterogeneous reaction system and related heterogeneous reaction systems are more in accord with solution chemistry than gas-phase ozonolysis. As will be described in the body of this dissertation, in the oleic acid–ozone heterogeneous reaction system, oleic acid can be viewed as the solvent and appears to affect the product identity and yields in accord with solution chemistry. In light of this, the following solvent effects should be noted:

- Product distributions (i.e. the types and/or relative yields of products) in solutions that are treated by ozonolysis often depend on the solvent \(^{244, 266-268}\).
- The presence and types of peroxidic products appears especially sensitive to the type of solvent \(^{243, 266, 269-272}\).
- Treatment of ozone-reacted mediums with acids \(^{244, 272, 273}\) may decompose ozonides and cause the formation of peroxyacids along with carbonyls. It is also well-established that bases can decompose ozonides and other peroxidic products of ozonolysis, forming ketones or aldehydes and carboxylic acids. Ozonolysis in
an aqueous medium can lead to the formation of $\alpha$-alkoxyalkyl hydroperoxides\(^{244}\), which can undergo decomposition \(^{244, 268, 274}\)

### 1.8. Photoelectron Resonance Capture Ionization Aerosol Mass Spectrometry

The purpose of the following section is to briefly introduce the novel methodology of photoelectron resonance capture ionization (PERCI) aerosol mass spectrometry (AMS) and associated aerosol generation and characterization equipment to the reader. An extensive description of PERCI-AMS is given elsewhere\(^{170-172}\) as are descriptions of aerosol generation and characterization equipment\(^{1, 4}\). Figure 1-2 is a general schematic of PERCI-AMS and associated aerosol generating and characterizing equipment.

Aerosols are generated by several common mechanisms: ultrasonic or pneumatic nebulization, or homogeneous nucleation from hot vapors. These aerosols are composed of polydisperse particles i.e. particles of different diameters. Particles are characterized by size by differential mobility analyzers (DMA). Polydisperse aerosol particles are charged by a radioactive bipolar charger in the DMA, and most particles under 300 nm in diameter will receive a single positive, negative, or zero charge in accord with the bipolar charge distribution\(^1\). Charged aerosol particles are separated in the DMA as a function of their electrical mobility, which is inversely proportional to particle size\(^1\). The DMA is usually used in conjunction with a condensation particle counter\(^1\) (CPC), which measures the number concentration of aerosol particles of a specific
diameter. Aerosol particles are detected by condensing a vapor (typically butanol) onto the particles converting them to droplets then are counted by an optical particle detector. Aerosols characterized in terms of size and number concentrations are then typically described by a size distribution, such as the log normal distribution\(^1\).

Aerosol particles can be reacted with a gas phase species (e.g. ozone) in a flow tube reactor. A flow tube reactor is typically constructed from two concentric glass tubes, with the inner tube acting as a movable injector\(^{172}\). The aerosol flow in the flow reactor is in the laminar regime, given by small Reynolds number\(^1\). The typical transit time of aerosol particles in flow reactors is on the time scale of seconds\(^{170,171,190}\).

Aerosol sampling inlets in AMS have two main functions. Firstly, the inlet facilitates the introduction of the atmospheric pressure aerosol particles into the ionization region of the mass spectrometer\(^42\), which has typical vacuum pressure in the range of \(10^{-5} - 10^{-7}\) torr\(^{170-172}\). Secondly, aerosol sampling inlets concentrate the particle component of the aerosol while pumping away the gaseous component\(^42\). This is typically achieved by passing the aerosol through 2 or 3 pressure stages that are separated by flow limiting orifices. As the aerosol passes through one stage to the next there is a pressure drop; subsequently, the aerosol expands into the lower pressure stage. During the expansion the lower mass gas molecules diverge and are pumped away, conversely the more massive particles have more momentum and are carried along the central axis of the particle inlet.
The novel component of PERCI AMS is the ionization source (Fig. 1-3). PERCI is based on the laser-induced photoelectric effect, to generate low energy (0-1 eV)\textsuperscript{170-172} photoelectrons. The photoelectron energy used in PERCI is nominally the difference in energies of the metal work function and the photon striking the metal surface\textsuperscript{170-172}. Aerosol particles are deposited on a vaporization probe that is placed in close proximity (~1-2 mm) to a metal photocathode (e.g aluminum). Vapors of the analyte evolve while low energy (sub-mJ) pulsed (10 Hz), tunable (235 – 300 nm) ultraviolet radiation is focused onto the surface of the metal photocathode generating short pulses (~ 5 ns) of photoelectrons\textsuperscript{170-172}. Vaporization of the organic analytes can be done by flash vaporization or by programmed ramping of the vaporization probe\textsuperscript{171}. The low energy of the photoelectrons constitutes the softness of the ionization process that is observed with PERCI, with two common modes of ionization being described: associative\textsuperscript{170} and dissociative\textsuperscript{170-172}. In the associative electron attachment (AEA) ionization process the analyte (AB) is ionized without fragmentation\textsuperscript{170}: \[
AEA \quad AB(gas) + e^- \rightarrow AB^-(gas)
\]

In dissociative electron attachment (DEA) there is fragmentation of the analyte:

\[
DEA \quad AB(gas) + e^- \rightarrow A(gas) + B^-(gas)
\]
For many organic compounds this type of fragmentation simply involves the loss of a (neutral) hydrogen atom, which is the case with organic acids\textsuperscript{171-172} that are the focus of the research presented in this work. Other modes of DEA ionization of organic molecules have been described, such as the loss of NO\textsubscript{2} by nitrobenzene derivatives as reported by LaFranchi and Petrucci\textsuperscript{170} and references therein.

Finally, mass analysis is done by time-of-flight mass spectrometry, operating in the reflectron mode. The ion extraction zone is in a Wiley-McLaren arrangement and employs delayed pulse ion extraction. The ion extraction electrodes are held at ground while the ionization laser is fired and then pulsed using a digital pulse generator. Typical delay times are from 0.1 – 10 microseconds\textsuperscript{170-172}. Data is acquired on a digital oscilloscope that is triggered by the digital pulse generator, triggering the oscilloscope simultaneously with the pulsing of the ion extraction electrodes.
1. Aerosol Generation: Form particles by nebulization or other mechanism.

2. Particle Counter and Sizing: Differential Mobility Analyzers (DMA) and Condensation Particle Counters (CPC) determine aerosol distributions by mass or number.

3. Ozone Generator: Ozone is generated by electric discharge and its concentration determined by spectrophotometry.


5. Particle Inlet: Introduces particles into ionization region while pumping away gases.

6. Ion Source: Ions are formed by attachment of low energy electrons to thermally vaporized organics from the aerosol.

7. Mass Spectrometer: Utilizes time-of-flight of negative ions to get mass information and discern chemical processing of aerosols.

Figure 1-2. General schematic of PERCI-AMS.
Figure 1-3. PERCI-AMS: closeup of ionization region, particle sampling inlet, and flight tube.

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2. Photoelectron Resonance Capture Ionization-Aerosol Mass Spectrometry of the Ozonolysis Products of Oleic Acid Particles: Direct Measure of Higher Molecular Weight Oxygenates

2.1. Introduction

Organic compounds are established as being ubiquitous components of atmospheric aerosols, comprising up to 50% of the total particulate mass depending on location and aerosol type\(^1\), \(^2\). Aerosol particles, including organic particles and those containing an organic component, are involved in the regulation of the planetary albedo \(^3\). The diameter of many particles in ambient aerosol is on the order of visible light, which is the regime that Mie scattering becomes significant. Mie scattering is a function of the refractive index of the material, which depends on the chemical composition\(^4\). Furthermore, in recent years, organic aerosols have been recognized as a potential sink for important atmospheric oxidants, such as ozone. As organic particles react with environmental gases the refractive index of the aerosol can change and subsequently the scattering properties of the particle can change as well. In addition, the hygroscopicity of organic particles may increase considerably as a result of heterogeneous atmospheric chemical reactions, impacting the ability of these otherwise hydrophobic particles to effectively act as cloud condensation nuclei (CCN) \(^5\).
As of late, 9-octadecenoic acid (oleic acid) in the particle phase reacting with ozone has emerged as the model system in trying to unravel the complexity associated with the heterogeneous chemistry and microphysics of organic aerosols in the troposphere. Oleic acid is a common monounsaturated fatty acid in the troposphere having both biogenic and anthropogenic sources. For example, concentrations of the level of 1 ng m$^{-3}$ have been measured in the remote marine environment$^2$. A great deal of effort has gone into measuring the uptake coefficient of ozone in oleic acid particles$^6$-$^10$, to elucidate the atmospheric impact of organic particles as ozone sinks. This is an especially important question in polluted environments where episodic ozone levels can reach hundreds of ppb$^4$,$^11$ and in the presence of elevated concentrations of organic particles. It should also be noted that recent density-functional theory calculations$^{12}$, suggest that intermediates associated with the ozonolysis of oleic acid in the presence of water may act as a significant source of small, reactive molecules such as hydroxyl radicals and various hydroxyalkyl hydroperoxides.

It is clear that the identity of the products generated by the reactions of organic particle phases, such as oleic acid, with oxidizing trace gases is of importance both in understanding the tropospheric carbon cycle and the cycles of many oxidizing species. Most methods of analysis of organic particulate are off-line and suffer from extended collection and analysis times and can be prone to sampling artifacts$^{13}$-$^{18}$. These disadvantages have recently prompted a push to the development of on-line methods$^{19}$ for the analysis of organic particles.
We have developed a method, photoelectron resonance capture ionization (PERCI) in conjunction with time-of-flight aerosol mass spectrometry (AMS) \textsuperscript{20, 21}, which is based on the capture of low energy electrons that are generated by a laser-induced surface photoelectric effect. Ionization occurs by an associative or dissociative electron attachment mechanism (AEA or DEA, the latter typically involving the loss of the hydrogen atom) when a low-energy electron is resonantly or near-resonantly attached to an organic molecule in proximity to the photocathode source. PERCI is an exceptionally soft and tunable method of ionization that minimizes the extensive fragmentation common to conventional electron impact ionization.

In this work, we describe the application of PERCI-AMS to the direct, on-line chemical analysis of the ozonolysis of ultrafine oleic acid particles. In addition to the ability to simultaneously measure all four classical ozonolysis products, we use PERCI-AMS to measure higher mass oxygenates, which may play a chemical role in more complex atmospheric organic particles. Our method permits, for the first time in the particle phase, the direct and simultaneous measurement of a plethora of higher order oxygenates, such as trioxolanes and peroxides that are in accord with the Criegee mechanism \textsuperscript{22}. The measurement of these higher order oxygenates permits us to postulate chemical mechanisms leading to their formation and the formation of the four major products observed by others.
2.2. Experimental

Ozone is generated by passing air through an electric discharge ‘ozonator’ (Mathesen 8340). The concentration of ozone is determined by passing the air-ozone mixture through a 10.0 cm quartz cell (NSG Precision Cells, Inc. 34) that is part of a photometer with a mercury discharge lamp (Spectroline 11SC-1) and a photomultiplier tube (Oriel Instruments 70680) with an accompanying monochromator (Oriel Instruments, 77250). The photometer is calibrated by using the 253.65 nm mercury line.

The ozone is then introduced into a 2.54 cm inner-diameter glass flow reactor upstream of a movable, concentric aerosol injector, which is another glass tube of 1/8-inch inner diameter. The gas flow is laminar (Re < 100) at one atmosphere total pressure and a partial pressure of ozone of about $1.8 \times 10^{-4}$ atm. Note that the ozone concentration used in these preliminary studies is greater that that used in previous reports 6-10, potentially affecting the chemistry, for example yielding a modified product distribution.

Oleic acid was purchased from Fisher Scientific Company (Fairlawn, NJ) and used without further purification. The particle phase was generated by pneumatically nebulizing oleic acid with a water/ethanol mixture (85:15, v/v) and passing the aerosol through a diffusion drier to remove water from the particles. As determined by a differential mobility analyzer (TSI 3080) coupled with a condensation particle counter (TSI 3010, TSI, Inc., Shoreview, MN), the size distribution of the dried aerosol was
found to have a geometric mean of 155 nm with a geometric standard deviation of 2.00. Particle number densities were on the order of $10^5$ cm$^{-3}$. The oleic acid particles are then introduced into the flow reactor via the inner injector tube. The particles then react with the ozone in the end of the flow reactor proximal to an aerodynamic particle inlet that connects the flow reactor with the ionization region of the mass spectrometer. The reaction time between the ozone and oleic acid particles is determined by the distance from the end of the injector tube to the particle inlet sampling port and gas flow rates. Typical reaction times are from 1 to 10 seconds.

After traveling through a particle inlet, discussed in detail elsewhere $^{23}$, reacted particles are deposited on a heated Nichrome filament that is in the flight path of the particle beam and in proximity (< 1cm) from the aluminum photocathode in the ionization region of the mass spectrometer. The particles are then vaporized by resistively heating the Nichrome wire to temperatures not exceeding 500 °C (an accurate measure of the temperature was not possible in these preliminary experiments), and ionized by low-energy (~0 eV) electrons. The PERCI photocathode is illuminated by pulsed ultraviolet radiation from an optically pumped parametric oscillator (Vibrant, Opotek Inc., Carlsbad, CA). The wavelength of the light used to generate the photoelectrons was 270 nm, with a 7 ns pulse width. The measured quantum efficiency is $6 \times 10^{-4}$ photoelectrons/incident photon, with photoelectron fluxes up to $10^{21}$ cm$^{-2}$s$^{-1}$. The flight chamber is an electrostatic reflector (reflectron) with a path length of 1.6 m. A depiction of the PERCI-AMS and further details are described elsewhere $^{20,21}$. 

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2.3. Results and Discussion

Figure 2-1 shows the PERCI mass spectrum of reaction products from the ozonolysis of oleic acid particles. The mass spectrum clearly reveals four major [M-H]⁻ ions, at m/z values of 141, 157, 171 and 187, that are the anticipated classical products associated with the decomposition of the 1,2,3-trioxolane (primary ozonide), shown in Scheme 2-1.

![PERCI mass spectrum of ozonolysis products of oleic acid.](image)

Although these four products have been observed independently in separate studies⁶⁻¹⁰,²⁴, it is only in this work and the recent work by Hearn and Smith²⁵ using
chemical ionization mass spectrometry, that they are all observed simultaneously as the unfragmented molecular ions. The relative product yields reported here for these four products is not in keeping with previous work \(^6\text{--}^{10}, \text{24}\). Specifically, the apparent yields of nonanal and 9-oxononanoic acid, which are relatively volatile, are higher than previously reported. Furthermore, such a high relative yield of azelaic acid (\(\text{HO}_2\text{C(CH}_2\text{)}_7\text{CO}_2\text{H}\)) has never been reported for similar reaction conditions. The explanation for these high relative yields may lay with the higher PERCI efficiency of the dicarboxylic acid moiety, as compared to the other three less extensively oxygenated products, or with decomposition of the lower volatility, higher molecular weight products, such as the secondary ozonides and geminal diperoxides, discussed below. For example, decomposition of the proposed ozonolysis products at 330, 346, and 360 u could lead to formation of azelaic acid or 9-oxononanoic acid, depending on the specific decomposition pathway. Furthermore, decomposition of the anhydride at 312 u could lead to formation of 9-oxononanoic acid and nonanal or nonanoic acid and nonanedial. Evidence for the second decomposition pathway is supported by a small ion signal at 155 m/z, corresponding to the nonanedial. Experiments are underway to calibrate the PERCI-AMS instrument for the known and proposed products of oleic acid ozonolysis to elucidate product evolution and explain the product yields observed in this work. Suitable standards for the proposed secondary ozonides and geminal diperoxide standards are not commercially available and their synthesis and isolation has not been reported in the literature. Nonetheless, as a first step, compounds with similar functionalities, such as cumene hydroperoxide and lauroyl peroxide, are being used to gain some insight into the
softness of the PERCI technique for these compound classes and to obtain a first order estimate of the sensitivity.

Scheme 2-1. Three-step reaction sequence for classical ozonolysis of alkenes adapted to oleic acid. Step 1 is the formation of the primary ozonide; step 2 is the decomposition of the primary ozonide by cleavage across bonds “a” and “b” and “c”; and step 3 is an example of possible dipolar cycloaddition (for ac-cleavage products) of Criegee intermediate (I) to an aldehyde.
The assignment of ion peaks in the PERCI mass spectra reported here is based on our previously published PERCI mass spectra of organic standards containing aldehyde, ketone, or carboxylic acid functional groups\textsuperscript{20, 21}. In analyzing these standards, it was found that in all cases the [M-H]\(^-\) peak was the most abundant peak, and is used in most cases in this work as the identifying peak for molecular products. Other minor peaks were observed such as the [M-OH]\(^-\) fragment in the case of aldehydes or ketone-containing molecules. In addition to our work, there is precedent in the literature\textsuperscript{26} for electron capture (using more conventional methods for electron generation) of some of these types of molecules has presented work specifically looking at fragmentation patterns of saturated and unsaturated fatty acids, finding, as we do, that the [M-H]\(^-\) peak is the dominant peak. For clarity, all ensuing discussion will refer to detected species as the original parent molecule, i.e., prior to ionization by PERCI. Also seen in the mass spectrum are higher mass ion peaks, tentatively assigned to other chemical products not observed previously to result from the heterogeneous ozonolysis of oleic acid particles.

It must be noted that the vaporization source used in these experiments presents an obstacle to providing quantitative measurements. Experimental parameters necessary for such measurements, including filament temperature, particle deposition efficiency, and vaporization efficiency, cannot be controlled accurately with this first-generation source. As a result, quantitative analysis of product yields was not possible at this stage of the work. Efforts are presently underway to calibrate the PERCI-AMS instrument with standards of the expected and proposed ozonolysis products.
The ensuing discussion is presented with the caveat that all experiments were conducted under dry laboratory conditions; however, real atmospheric particles are known to be complex chemical mixtures containing a multitude of components, including water, organics, and salts. Therefore, the chemical products resulting under dry laboratory conditions may differ from those obtained in the atmosphere. For example, in the gas phase\textsuperscript{27, 28}, it has been shown that water vapor reacts with the Criegee intermediates. Furthermore, results presented here suggest that the Criegee intermediates can react rapidly with other organics, such as aldehydes, native to the particle.

The three principal steps associated with the ozonolysis of an alkene all involve 1,3-dipolar reactions\textsuperscript{22, 29, 30}. Scheme 2-1 shows these steps for the specific case of oleic acid. Step 1 involves formation of a primary ozonide that is typically unstable\textsuperscript{22}. This ozonide rapidly decomposes by two distinct routes. The ac-cleavage route nominally gives nonanal (142 u) and a carboxylic acid zwitterion (I) with a carbonyl oxide end (Criegee intermediate) at 188 u. Similarly, the bc-cleavage route gives 9-oxononanoic acid (172 u) and another Criegee intermediate (II) at 158 u. Especially in the gas phase, the Criegee intermediates are short lived\textsuperscript{31} and are known to rapidly rearrange\textsuperscript{32-34}; molecular assignments at 188 u and 158 u, then, are invariably made to the corresponding acids, azelaic acid and nonanoic acid. In the condensed phase, Criegee intermediates are longer lived due to more rapid thermalization. It is possible therefore, that the Criegee intermediates will undergo cycloaddition with the corresponding aldehyde produced in Step 2 to produce the 1,2,4-trioxolanes (secondary ozonides), as predicted by Criegee\textsuperscript{22}. 

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and shown in Step 3 of Scheme 2-1. Further, rearrangement and reaction of the Criegee intermediates is possible, some examples of which are shown in Scheme 2-2.

We represent the carbonyl oxide intermediates (I and II) as zwitterions, in accord with Criegee’s initial description. Although there is considerable theoretical evidence for carbonyl oxides, to the authors’ knowledge, they are difficult to isolate and have been directly observed for other chemical systems only by matrix-isolation techniques. We have chosen to focus on one specific resonance form of the zwitterion, of the several other forms that have been proposed, although these Criegee intermediates can also exhibit reactivity characteristic of biradicals, especially in the gas phase. These highly reactive intermediates greatly enrich the variety of chemical reactions and products possible.
Simplistically, one would expect an equal yield of the four major chemical products from the second step of ozonolysis. However, there exists a plethora of potential mechanistic pathways by which these products can be formed, significantly skewing product yield distributions. For example, Scheme 2-2 shows an abbreviated set of possible reactions for one of the intermediates (II), with at least four different pathways shown leading to the formation of nonanal.

It is important to stress that in chemically complex atmospheric particles; the operative pathways will depend on the chemical composition of the particle, and may also depend on the location of the reaction on the particle, i.e., surface vs. bulk. Therefore, the majority of the possible pathways cannot be discarded based on observations from this simple chemical system.

In accordance with previous studies\textsuperscript{6, 24, 25}, we assign the peaks at 157 u and 187 u to nonanoic acid and azelaic acid respectively. Although formation of the acid is usually stated simply to proceed by an internal rearrangement of the Criegee intermediate\textsuperscript{25} to the authors’ knowledge no plausible mechanism has been given for the specific case of oleic acid. We propose an extension of the rearrangement mechanism given by Cremer et al. \textsuperscript{33} for carbonyl oxide, CH\textsubscript{2}OO. In this mechanism, a rearrangement of the Criegee intermediate (II) to the corresponding acid may proceed via a cyclization reaction to the dioxirane, followed by a rapid H transfer to the oxygen, forming the acid as shown in Scheme 2-2. This mechanism is supported by coupled-cluster with single and double excitations (CCSD) calculations on carbonyl oxide, CH\textsubscript{2}OO, which infers that the dioxirane is more thermodynamically stable than the Criegee intermediate and that
the acid is more stable than both. It should be noted that the first step, i.e., formation of
the cyclic dioxirane, is photochemical\textsuperscript{34, 37, 38}. For the case of CH\textsubscript{2}OO, wavelengths longer
than 300 nm are absorbed by the carbonyl oxide and cause the formation of the dioxirane
and other products. The photochemistry of diphenylmethylene oxide (\(\lambda > 630\) nm)\textsuperscript{38} and
\(p\)-benzoquinone oxide (\(\lambda > 630\) nm) \textsuperscript{37} to the corresponding dioxiranes has been
documented.

The exceptionally soft nature of PERCI also permits measurement of a host of
higher mass trioxolanes, peroxides and similar products. These highly oxidized
compounds may arise from 1,3-dipolar additions of the Criegee intermediates with the
carbonyl groups. As shown in Figure 2-2, a number of higher mass peaks with m/z of
281, 285, 299, 301, 311, 313 and 315 are observed.

![Figure 2-2. Expanded region of the PERCI mass spectrum shown in Figure 2-1, highlighting the higher molecular weight oxygenates.](image)

The 281 m/z is the [M-H]\textsuperscript{-} ion of oleic acid. The 285 m/z is likely the [M-H-CO\textsubscript{2}]\textsuperscript{-}
of the 1,2,4-trioxolane formed by the dipolar addition of the Criegee intermediate to the
aldehyde (Step 3, Scheme 2-1). We refer to this as the ‘conventional’ addition product, since, as discussed by Loan et al.\textsuperscript{30} the addition of the Criegee intermediate with a carbonyl moiety can proceed by two main routes: a) the addition of the two members from the same cleavage route (i.e. nonanal with the 188 u Criegee intermediate from the ac-cleavage route, see Step 3 in Scheme 2-1), b) addition of the aldehyde from one cleavage pair with the Criegee intermediate from the other cleavage pair (i.e. 9-oxononanoic with the 188 u Criegee intermediate of the ac-cleavage route). The former process will yield the conventional secondary ozonide, the latter yields cross ozonides. The mechanism of crossing over for oleic acid is presented in Scheme 2-3 for the two cleavage routes.

In accord with this proposed mechanism, the mass of 300 u is a cross ozonide formed from the addition of nonanal and the Criegee intermediate (II) formed by the bc-

![Scheme 2-3. Cross ozonide products.](attachment:image.png)
cleavage route. We observe a peak at 299 m/z, which we propose is the [M-H]⁻ for this secondary ozonide. By a similar argument we propose that the 315 m/z may be the [M-H-CO₂]⁻ cross ozonide arising from the dissociative ionization of the addition product of 9-oxononanoic acid with the Criegee intermediate (I) from the ac-cleavage route. However, as shall be discussed below, this assignment is tentative, because there is a 1,2,4,5-tetraoxane (commonly referred to as a cyclic geminal diperoxide) of similar mass that could arise from the dissociative electron capture of two bc-route Criegee intermediates undergoing cycloaddition (i.e., II + II).

As shown by Criegee and Loan et al. 22, 30 with simple alkenes, two carbonyl oxide zwitterions may dimerize forming a cyclic geminal diperoxide, illustrated in Scheme 2-4.

Support for this pathway is also provided by Hearn and Smith 25 who invoke it to explain the production of excess 9-oxononanoic acid. They did not observe the geminal diperoxide, but rather the decomposition products nonanal and 9-oxononanoic acid. Here, we have assigned several lower intensity peaks in the higher m/z portion of the spectrum.

Scheme 2-4. (a) Homo- and (b) hetero-cyclic geminal diperoxides formed from Criegee intermediates.

Support for this pathway is also provided by Hearn and Smith 25 who invoke it to explain the production of excess 9-oxononanoic acid. They did not observe the geminal diperoxide, but rather the decomposition products nonanal and 9-oxononanoic acid. Here, we have assigned several lower intensity peaks in the higher m/z portion of the spectrum.
to geminal diperoxide products. The 301 m/z is proposed to be the dissociative ion, [M-H-CO$_2$]$^-$, of VII, formed from the dimerization of the two different Criegee intermediates (i.e., I + II). The 315 m/z is proposed to be the DEA ion, [M-H]$^-$, that arises from the dimerization of the Criegee intermediates from the bc-cleavage route (i.e., II + II). An ion peak at 331 m/z, corresponding to the [M-H-CO$_2$]$^-$ DEA product from dimerization of the Criegee intermediate from the ac-cleavage route (i.e., I + I), is not observed. The aforementioned cyclic geminal diperoxide that would result from the dimerization of I + I from the ac-cleavage route is a dibasic acid; the relatively high polarity of the acid functional groups would greatly decrease its vapor pressure. Since PERCI requires a preliminary vaporization of the organic compound, the dibasic acid in question may simply not be volatile enough to be thermally vaporized at the temperatures used in this work. As noted, we commonly observe the loss of a mass 45 u (and in fact observe strong 45 m/z ion signals in these experiments) with organic acids; we postulate that the ion signal observed at 143 m/z is in effect the dianion that arises from the loss of 90 mass units, [M-2H-2CO$_2$]$^-$. It must be noted that the 143 m/z could also arise from the loss of H and CO$_2$ from the ac-cleavage route Criegee intermediate (I) or its corresponding dicarboxylic acid, azelaic acid.

We also observe an ion signal at 311 m/z, which we postulate to form from the addition of 9-oxononanoic acid to Criegee intermediate (II), as shown in Scheme 2-5. This pathway leads to a hydroperoxy moiety in the $\alpha$ position to the oxygen of an ester group, which upon dehydration gives a product of mass 312 u. Subsequent DEA yields the observed 311 m/z.
The 313 m/z is proposed to form via a radical-initiated reaction involving the 141 u species and 9-oxononanoic acid, as shown in Scheme 2-6. The 141 u species can be either the DEA product of nonanal or arise from the Criegee intermediate (II) via the hydroperoxy alkyl that undergoes homolytic cleavage as shown in syn pathway in Scheme 2-2. Note that the initial radical, i.e., 141 u, is not consumed, but rather propagated. It is not unreasonable to expect that the radical formed will undergo associative electron attachment, producing the more stable condensed-phase ion.
2.4. Conclusion

PERCI-AMS has afforded a clearer picture than has been previously possible regarding the ozonolysis of environmentally relevant monounsaturated fatty acid particles, such as oleic acid. The novel spectrometric technique has been used to identify the four major products associated with the second step of ozonolysis of oleic acid: nonanal, nonanoic acid, 9-oxononanoic acid, and azelaic acid. The softness of the PERCI technique minimizes fragmentation compared to harder ionization techniques (i.e., electron impact ionization) producing simple and rich mass spectra that also permit the
identification of a self-consistent set of higher molecular weight compounds including 1,2,4-trioxolanes, which are products of both conventional and cross cycloaddition of the Criegee intermediates and aldehydes. Other higher molecular weight compounds are proposed to be 1,2,4,5-tetraoxanes (cyclic geminal diperoxides), the latter being proposed to form from the dimerization of the Criegee intermediates. To our knowledge these higher molecular weight cyclic oxygenates have not been directly observed in prior particle-phase ozonolysis experiments of oleic acid, or other atmospherically relevant unsaturated fatty acids. A number of these products, as well as others, have, however been identified in bulk liquid phase ozonolysis experiments using NMR\textsuperscript{43}. These oxygenates, summarized in Table 2-1, are suggested to be most of the 1,3-dipolar cycloaddition products arising from reactions of the Criegee intermediates and may have significant ramifications on the chemistry and physics of the troposphere. These ramifications include, but are not limited to, the particles being a source of radicals as well as enhancing the fatty acid particles’ propensity towards acting as CCN.

2.4.1. Chemical Implications to the Troposphere

The reaction of oleic acid particles with ozone leads to high volatility products, such as nonanal and less-volatile species including nine-carbon organic acids and perhaps some very low volatility, high-molecular weight cycloaddition products, which are probably bound to the liquid phase under atmospheric conditions. All the proposed cyclic structures share the commonality of the oxygen-oxygen bond, which under
environmental conditions may act as a source of highly reactive alkoxy radicals, RO\textsuperscript{44}. Also, the proposed rearrangement mechanisms from 1,2,4-trioxolanes to peroxides may provide a pathway to the formation of hydroxyl radical. The contribution of hydroxyl radical from the suggested pathway to atmospheric levels however, remains to be evaluated. Previous studies have indicated that ozonolysis of gas-phase alkenes leads to the production of OH radical\textsuperscript{31,41,45-51}; however, the production efficiency decreases with alkene size\textsuperscript{52}. In addition, in condensed phase reactions, OH does not form from monolayer reactions\textsuperscript{52}. Nonetheless, attempts are underway to model the extent to which anthropogenically generated alkenes contribute to atmospheric HO\textsubscript{x} levels\textsuperscript{12, 53}. The theoretical studies thus far indicate that the ozonolysis of atmospheric alkenes may be an important contributor to the dark season tropospheric oxidant content. It seems natural therefore, to extend these experimental observations and theoretical predictions to the ozonolysis reactions of oleic acid particles, in spite of the molecule’s relatively long chain length.

While it is intriguing to consider the possibility of particle phase reactions potentially contributing to the dark season gas phase OH levels, we have no data to postulate the significance, if any, of such a contribution. We are convinced however that the possibility of the in situ production of OH within the particle must be taken into account in the analysis of particle phase ozonolysis of alkenes. In this study, although we did observe a strong signal at m/z 17, which appears to be correlated to the extent of ozonolysis, a high background signal at this same m/z precluded any conclusive statements.
The evidence of cycloaddition of the products of the second step of ozonolysis, especially the proposed cross ozonation, infers the rich and viable reactivity that these fatty acid mediums provide. Small, mobile atmospherically relevant aldehydes, such as formaldehyde and acetaldehyde, both species of environmental concern, could undergo cycloaddition with Criegee intermediates and effectively be “trapped” in the form of cyclic trioxolanes. These high-molecular weight compounds would have much lower volatility than the aldehydes; hence oleic acid and other unsaturated compounds in the particle phase could be a tropospheric sink for such species. This type of reaction has been observed in the bulk liquid phase\textsuperscript{30, 54}. Upcoming experiments in our group will place emphasis on the observation of such reactions in the particle phase.

2.4.2. Physical Implications in the Troposphere

The second step of ozonolysis of an unsaturated fatty acid, such as oleic acid, increases the number of hydrophilic groups from one (the initial carboxylic acid) to three. Also, the formation of high-molecular weight groups with low vapor pressure partitions polar functional groups (peroxides, trioxolanes, etc) to the particle phase. These combined factors will directly increase the particles hygroscopicity, which could increase the particles ability to act as a cloud condensation nucleus\textsuperscript{55-59}.

The microphysics of this process has global implications due to the ubiquitous nature of fatty acids such as oleic acid. This may have significant implications in oceanic regions where it is estimated that up to 200 Tg yr\textsuperscript{-1} of organic carbon in the form of...
lipids, including fatty acids, is deposited at the ocean-air interface\textsuperscript{60}. These organic acids are ejected into the troposphere mechanically\textsuperscript{61, 62}, typically forming coatings of brine particles\textsuperscript{60}. Early suggestions were that such organic layers were inert\textsuperscript{63}, yet it was later pointed out that the hydroxyl radical could react with such surfaces changing optical, physical and chemical properties of the surface\textsuperscript{60}. We would like to point out that both direct ozonolysis, and its secondary reactions potentially exacerbate these effects by forming reactive products (such as radicals associated with the photolysis of various peroxides and the hydroxyl radical), and could therefore be another important facet of atmospheric processing in the marine boundary layer.

It should be kept in mind that oleic acid has been studied as a model system of unsaturated organic aerosol. The atmospheric relevance of the oleic acid-ozone system is not certain. As shown in this and other studies, the ozonolysis of even a simple one-component particle phase can lead to a variety of interesting products with potentially significant implications to both the chemical and physical environment. In future studies we will apply PERCI-AMS to more complicated and relevant, multi-component particle phases reacting with ozone and other trace gases. For example, it may be that sinking of the oxy-VOCs to the organic particle phase, as suggested in this work, may be of less significance in water-containing particles than in the lab studies performed here on pure, dry oleic acid particles. From these continuing studies we hope to not only observe the products from these more complex systems but also get a more realistic view of atmospheric processing of organic carbon in the natural troposphere.
### Table 2-1. Summary of reaction products from ozonolysis of oleic acid particles.

* Assignments specifically given in reference, whether conclusive or tentative; ≠ Assignment made based on predicted fragmentation; (a) Hearn and Smith⁶; (b) Katrib et al.²⁴; (c) Moise and Rudich⁸; (d) Morris et al.⁷; (e) Smith et al.³; (f) Thornberry and Abbott⁹; (g) This work; (h) These products are also possible by decomposition of the proposed higher molecular weight oxygenates.

<table>
<thead>
<tr>
<th>Parent molecule</th>
<th>u  (amu)</th>
<th>Observed ion* (m/z)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃(CH₂)₇CHO (Nonanal, NL)</td>
<td>142</td>
<td>141⁸,c,g, 142², 143ᵃ,i, 16ʲ, 179ʲ</td>
<td>(h)</td>
</tr>
<tr>
<td>CH₃(CH₂)₇CO₂H (Nonanoic acid)</td>
<td>158</td>
<td>157ᵍ, 158ᵇ, 159ᵃ</td>
<td>(h)</td>
</tr>
<tr>
<td>OHC(CH₂)₇CO₂H (9-oxononanoic acid, OX)</td>
<td>172</td>
<td>171ᶜ,g, 127ᵍ, 155ᵃ,c,g, 144ᵇ, 173ᵃ</td>
<td>[M-H-CO₂]⁻, (h)</td>
</tr>
<tr>
<td>HO₂C(CH₂)₇CO₂H (Azelaic acid)</td>
<td>188</td>
<td>187ᵇ, 189ᵃ, 152ᵇ, 143ᵍ</td>
<td>[M-H-CO₂]⁻, (h)</td>
</tr>
<tr>
<td>CH₃(CH₂)₇CH=CH(CH₂)₇CO₂H (Oleic acid)</td>
<td>282</td>
<td>282ᵈ, 281ᵍ</td>
<td></td>
</tr>
<tr>
<td>CH₃(CH₂)₈CO(CH₂)₇CO₂H</td>
<td>298</td>
<td>299ᵃ</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>299ᵃ</td>
<td>II + NL (cross ozonide)</td>
</tr>
<tr>
<td></td>
<td>312</td>
<td>311ᵍ</td>
<td>II + OX – H₂O</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>313ᵍ</td>
<td>See Scheme 2-6</td>
</tr>
<tr>
<td></td>
<td>316</td>
<td>315ᵈ</td>
<td>II + II</td>
</tr>
<tr>
<td></td>
<td>330</td>
<td>285ᵍ</td>
<td>[M-H-CO₂]⁻ of II + OX and I + NL</td>
</tr>
<tr>
<td></td>
<td>346</td>
<td>301ᵍ</td>
<td>[M-H-CO₂]⁻ of I + II</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>315ᵍ</td>
<td>[M-H-CO₂]⁻ of I + OX</td>
</tr>
</tbody>
</table>
2.5. References


23. Petrucci, G. A.; Farnsworth, P. B.; Cavalli, P.; Omenetto, N., A differentially pumped particle inlet for sampling of atmospheric aerosols into a time-of-flight mass


3. Direct Observation of Polymerization in the Oleic Acid-Ozone Heterogeneous Reaction System by Photoelectron Resonance Capture Ionization Aerosol Mass Spectrometry

3.1. Introduction

Organic surfactants are a major component of atmospheric particles\(^1\)\(^-\)\(^4\); however, our understanding of the role of particulate organics in atmospheric chemical and physical cycles is in its infancy. It has become clear that organic compounds are intricately tied to a myriad of atmospheric processes, such as cloud formation, oxidizing capacity, and radiative forcing\(^5\)\(^-\)\(^9\). Further, a general problem in environmental chemistry at this time is accounting for the fate of atmospheric carbon, particularly in the troposphere. Several recent studies have reported on the possibility of oligomer formation on atmospheric particles as a mechanism causing a greater-than-expected partitioning of otherwise volatile and semi-volatile organics to the particle phase\(^10\)\(^-\)\(^12\). A better description of the fate of atmospheric compounds in the presence of trace oxidizing gases is requisite therefore to develop a more complete understanding of the carbon cycle in the troposphere.

Fatty acids are a ubiquitous component of the organic fraction of atmospheric particulate. As such, the oleic acid-ozone reaction system has evolved as an important model for understanding the processing of monounsaturated fatty acids with trace oxidant
gases of significance to tropospheric chemistry. Oleic acid (9-octadecenoic acid) is present in both the pristine and polluted troposphere. Concentrations on the order of 1 to 100 ng m\(^{-3}\) have been measured in the remote marine and polluted environment respectively.

Heterogeneous reaction of oleic acid involves oxidative cleavage of the unsaturation at position nine of the carbon backbone. Although the oxidative cleavage of unsaturated compounds by ozone has been observed since the early part of the twentieth century, a more complete description of this reaction is needed to better understand cycling of organic compounds in the troposphere. The oxidative cleavage of the carbon-carbon double bond, or ozonolysis, has been shown to form a reactive medium that can be a source of free radicals, including hydroxyl radical. These radicals can undergo a host of secondary reactions including hydrogen abstraction and initiation of free radical reactions, as demonstrated in this work.

One class of the most important intermediates of ozonolysis is the carbonyl oxides, more commonly referred to as Criegee intermediates. These intermediates are formed in retro [3+2] dipolar cycloaddition of the 1,2,3-trioxolane, i.e., primary ozonide, that is the product of the addition of ozone to the carbon-carbon double bond. Criegee intermediates are highly reactive and can undergo O-atom elimination, ester and acid formation, and hydroperoxide formation. While these reactions are important in the gas phase, and are typically rationalized through the capaciousness of the biradical resonance of the Criegee intermediate, in condensed media the zwitterionic resonance forms are consistent with several important experimental observations. In the condensed
phase, concerted cycloaddition \([3 + 2 \rightarrow 5]\) typical of 1,3-dipoles has been observed. Scheme 3-1a shows the general mechanism of 1,3-dipolar cycloaddition between a Criegee intermediate \(^{35,36}\) (shown as the zwitterionic resonance) and a carbonyl moiety\(^{18,37-39}\). Scheme 3-1b shows a similar mechanism between two Criegee intermediates which is consistent with the observation of cyclic geminal diperoxide formation\(^{18,30,37,40}\).

![Diagram](image-url)

Scheme 3-1. General mechanism of (a) a Criegee intermediate undergoing 1,3-dipolar cycloaddition and (b) 1,3-dipolar cycloaddition of two Criegee intermediates forming a cyclic geminal diperoxide. In (a) \(R=\) alkyl; \(R’=H, OH; R”=H, alkyl\). In (b) \(R\) and \(R’\) are alkyl groups.

Products of 1,3-dipolar cycloadditions, namely 1,2,4-trioxolanes, i.e., secondary ozonides, and cyclic geminal diperoxides have been isolated at low temperature\(^{37,40}\); however, it was not until our recent work\(^{18}\) that these products were directly observed in the heterogeneous reaction of a particle-phase alkene, i.e., aerosol, specifically oleic acid, and gas-phase ozone. This observation is significant in that it shows that the Criegee
intermediates in this atmospherically relevant heterogeneous system behave in accordance to what has been observed in solution phase chemistry\textsuperscript{37, 39, 40}. To our knowledge, the branching ratio between these cycloaddition products and decomposition pathways has not yet been measured or modeled.

Another potential consequence of the formation of cyclic oxygenates in these heterogeneous systems is their capacity to act as initiators of free radical reactions by cleavage of the oxolane oxygen-oxygen bond\textsuperscript{41-43}. In the solution phase there is experimental evidence that secondary ozonides can act as initiators of these radical reactions. Importantly, as we show in our work, the presence of these cyclic oxygenates can initiate a cascade of events leading to the production of oligomeric species in atmospheric particles. The observation of cyclic oxygenated compounds and, upon further reaction, oligomers being produced in ozonized oleic acid aerosols naturally raises the question of their impact on the reactive uptake of trace tropospheric oxidant gases such as ozone.

The development of on-line, real-time methods of aerosol analysis has contributed greatly to our understanding of particle phase-gas phase reaction systems and has been applied to tropospheric chemistry\textsuperscript{44}. These methods have overcome many of the challenges inherent to off-line methodologies, including protracted collection and analysis times, and sampling artifacts\textsuperscript{45-50}.

We have developed a novel methodology for the on-line analysis of particle-bound organics (photoelectron resonance capture ionization, PERCI) which, coupled with
aerosol mass spectrometry (AMS) has facilitated the direct measurement of products of heterogeneous direct observations to the soft ionization afforded by PERCl$^{51,52}$.

In this work we describe, for the first time, the direct observation of polyanhydrides formed on aerosol particles in the oleic acid-ozone heterogeneous reaction system. A mechanism is proposed that involves addition of a Criegee intermediate to a carboxylic acid, forming an $\alpha$-acyloxyalkyl hydroperoxide, which dehydrates to the polyanhydride.

3.2. Experimental

Ozone is generated by passing USP medical air through an electric discharge ‘ozonator’ (Mathesen 8340). The concentration of ozone is determined spectrophotometrically by passing the air-ozone mixture through a 10.0 cm quartz cell (NSG Precision Cells, Inc., Farmingdale, NY) that is in line with a magnesium hallow cathode lamp and an echelle polychromator (ESA 3000, LLA Instruments GmbH, Berlin-Adlershof, Germany). Absorption of radiation at the 279.55 nm emission line of magnesium by ozone ($\sigma = 415.8 \times 10^{-20} \text{ cm}^2$) is used to determine the partial pressure of ozone flowing through the cell. The partial pressure of ozone during these experiments was $1.8 \times 10^{-4}$ (±0.2 $\times 10^{-4}$) atm.

The ozone flow is introduced into a 2.54 cm inner-diameter concentric glass flow reactor upstream of a movable aerosol injector, which is another glass tube of 1/8-
inch inner diameter. The gas flow is laminar (Re < 100) under the experimental conditions used for this work.

Oleic acid was purchased from Mallinkrodt Baker, Inc. (Paris, Kentucky) and used without further purification. The particle phase was generated by pneumatically nebulizing oleic acid in a water/ethanol mixture (85:15, v/v) and passing the aerosol through a diffusion drier to desolvate the particles. As determined with a Scanning Mobility Particle Sizer (Model 3936L10, TSI, Inc., Shoreview, MN), the size distribution of the dried aerosol was found to have a geometric mean diameter ($d_g$) of 202 nm with a geometric standard deviation ($\sigma_g$) of 1.97. Particle number densities were on the order of $10^5$ cm$^{-3}$. The oleic acid particles, introduced into the flow reactor via the moveable inner tube, react with the ozone in the flow reactor before being sampled. The reaction time of the oleic acid particles with the ozone gas is determined by the position of the inner aerosol injector tube within the outer flow reactor tube. Reaction times for this work were in the range 8.2 and 22.7 s. The flow rate through the reactor was determined to be 0.6 L min$^{-1}$, of which 0.45 L min$^{-1}$ were sampled into the PERCI-AMS and the remainder passed to waste. The PERCI-AMS system has been described in detail elsewhere$^{51,52}$ and only a brief description is provided here.

Particles are sampled into the AMS through a differentially pumped particle inlet which focuses them along the central axis of the inlet using aerodynamic lenses. The particles are then deposited onto a custom-built collection probe placed in the center of the ionization region of the mass spectrometer. The probe, which also serves as the vaporization source, consists of a tight coil made of 4 turns of a 30 AWG Nichrome wire
with an internal coil turn diameter of 2 mm. The coil is positioned in the flight path of the particle beam and in proximity (< 1 cm) to the aluminum photocathode in the ionization region of the mass spectrometer. Particles are vaporized by passing a current through the coil. The vaporized molecules are subsequently ionized by low-energy (~0 eV) electrons as the PERCI photocathode is illuminated by pulsed ultraviolet radiation from an optically pumped parametric oscillator (Vibrant, Opotek Inc., Carlsbad, CA). The wavelength of the light used to generate the photoelectrons was 270 nm, with a 7 ns pulse width. A reflectron time of flight mass spectrometer with pulsed ion extraction (RM Jordan, Grass Valley, CA) was used for mass analysis and mass spectral data was acquired using a LeCroy Wavepro 7000 (Chestnut Ridge, NY) digital oscilloscope running in a conditional triggering mode. When an ion is detected during any given laser pulse over a selected mass range (> 300 m/z), the mass spectrum from that laser pulse is saved. After the collected aerosol sample has completely vaporized and the gas has diffused away, the scope stops triggering, and a further aerosol collection sequence is begun.

For the experiments presented here, particles were allowed to accumulate for 5 minutes on the Nichrome coil (corresponding to a total sampled mass on the order of 10 μg per measurement), and were vaporized by resistively heating the coil. While the temperature of the heated coil was not known accurately, it could be reproducibly set at various applied currents to give a relative measure of the vaporization source temperature. Two current settings were used, 330 and 600 mA, yielding our “lower” and “higher” temperature mass spectra, respectively. A quick ramp of the vaporization
current is believed to be important in allowing the more thermally unstable compounds to vaporize before decomposing. Although accurate knowledge of the temperature is not necessary for the results presented here, we are in the process of incorporating this capacity into our PERCI-AMS instrument for future experiments.

3.3. Results and Discussion

After analysis of the mass spectra from the collected samples at high and low vaporization currents, it was apparent that the higher vaporization current leads to a significant enhancement of the many high molecular weight (\(~ 300-1000 \text{ m/z}\)) ions. This was the case at both ozone exposure times. The lower vaporization current, however, was ideal for observing the 4 classical oleic acid ozonolysis products (azelaic acid, 9-oxononanoic acid, nonanoic acid, and nonanal) as well as other more volatile products, including peaks at 209 and 297 m/z. In looking for oligomer formation from the ozonolysis of oleic acid, therefore, we focused on the high temperature mass spectra. The two mass spectra that are referenced in the ensuing discussion of the oligomer formation from the ozonolysis of oleic acid particles were acquired under the following experimental conditions. The PERCI mass spectrum in Figure 3-1 was measured after an ozone exposure time of 22.7 s. The collected particles were then vaporized with a heater current of 660 mA. The inset is an expanded view of the higher mass region.
Figure 3-1. Higher mass region of the PERCI mass spectrum of the ozonolysis products of oleic acid particles indicating oligomer formation. The reaction time is 22.7 s. Inset is a x 10 expansion (in intensity) of the higher mass region indicating oligomer formation.

Note that the instrument response has not been calibrated for all measured chemical components, nor has consideration been given to any bias in the sensitivity that might result across the total measured mass range. Although such biases are not critical to the conclusions presented here, such calibrations are underway to permit quantitative measurement of chemical kinetics and product yields. The spectrum in Figure 3-2 on the other hand, was acquired from an aerosol that had been exposed to ozone for only 8.2 s and the collected aerosol was vaporized in this case at only 330 mA.
Figure 3-2. PERCI mass spectrum of classical products from the ozonolysis of oleic acid particles. The reaction time is 8.2 s.

We have highlighted therefore the two extremes in the experimental conditions: at the longer exposure time with vaporization suited for enhancement of high molecular weight products and at the short exposure time under conditions suited for the enhancement of lower molecular weight products.

In an earlier work we proposed a mechanism by which a Criegee intermediate and carboxyl group could react to form an $\alpha$-acyloxyalkyl hydroperoxide, which dehydrates \textit{in situ} to form an anhydride\textsuperscript{18}. This mechanism was consistent with a 312 U ozonolysis product observed by PERCI-AMS. A general form of this mechanism is shown in Scheme 3-2. Recent emphasis in our laboratory has focused on the detection of oligomeric and polymeric products formed in and/or on atmospheric particles. As we
show below, oxidation of unsaturated fatty acids by heterogeneous reaction with atmospheric ozone can lead to high molecular weight products and may be a significant source of low volatility, highly reactive oxygenated carbon in the atmosphere.

As shown in the PERCI mass spectrum of the heterogeneous ozonolysis products of oleic acid (Figure 3-1), chemical products are formed at 451.3, 621.4, and 791.5 m/z. As discussed in a previous report, because PERCI proceeds by a dissociative electron attachment mechanism\textsuperscript{51, 52}, we assign the nominal masses of the observed products to 452.3, 622.4, and 792.5 U, respectively. Proposed structures for these high-mass ozonolysis products of oleic acid are shown in Scheme 3-3.

The difference in nominal mass of these products is 170.1 U, which corresponds to C\textsubscript{9}H\textsubscript{14}O\textsubscript{3}. We herein propose this is in accord with the mechanism given in Scheme 3-4a, in which the Criegee intermediate (I) undergoes addition to oleic acid forming an \( \alpha \)-
acyloxyalkyl hydroperoxide (III or IV). Further, polymerization can continue at the remaining, unreacted carboxylic acid retained in intermediate III (Scheme 3-5).

![Scheme 3-3. Proposed structures of polymeric products of ozonolysis of oleic acid particles observed by PERCI mass spectrometry in a heterogeneous reaction system.](image)

The products at 452.3, 622.4, and 792.5 U, respectively represent the first three additions of I to oleic acid, forming $\alpha$-acyloxyalkyl hydroperoxides, with subsequent dehydration to the anhydride. The product corresponding to the addition of a fourth Criegee intermediate I was also observed, albeit at lower signal intensity, in the mass spectrum at 962 m/z. Higher molecular weight polyanhydrides were not observed, perhaps due to the limited reaction times possible with the existing flow reactor.
The addition product of Criegee intermediate II to oleic acid was also observed in this work (Scheme 3-4b). This addition product was recently observed by HPLC-MS and infrared spectroscopy\textsuperscript{14}, and by aerosol chemical ionization mass spectrometry\textsuperscript{13}. In this reaction, addition of II which has an alkyl end group, acts as a terminating agent to further polymerization.

Scheme 3-4. General schemes showing proposed addition of Criegee intermediates a) I and b) II to oleic acid.

Hung et al.\textsuperscript{14} describe this mechanism up to the formation of the α-acyloxyalkyl hydroperoxide having nominal mass 440 U. This corresponds to a 422 U anhydride upon dehydration. A multiplet of ion signals is observed in our mass spectra at 421 m/z, where the ion produced by PERCI is expected. The intensity of this ion signal is less than the ion signal associated with oleic acid + I, which is counterintuitive. The latter case has the
capacity to undergo further polymerization, which would diminish the intensity of the 451 m/z signal; however, this observation may relate to the ionization efficiency of the acid (oleic acid + I) vs. the anhydride with the alkyl end groups (oleic acid + II).

Scheme 3-5. Generalized polymerization scheme proposed for the addition of Criegee intermediate I to oleic acid. Note that the addition of Criegee intermediate II at any juncture (indicated by solid circles) would result in termination of the polymerization process. Underlined products were observed directly in the PERCI mass spectrum.

At the shorter reaction time, in addition to the four classical ozonolysis products of oleic acid, ion signals are also observed at 209 and 297 m/z (Figure 3-2). The product ion at 209 m/z is the sodium adduct of azelaic acid. This has been confirmed in a separate experiment in which the potassium adduct was readily formed and measured by
nebulizing a solution of azelaic acid in 1 ppm KI. Under similar concentrations of ozone and oleic acid, but shorter reaction time, as discussed above, another addition product with molecular weight greater than oleic acid is measured at 297 m/z. We assign this signal to 9- or 10-oxooctadecanoic acid, with the former isomer predicted in this system by Katrib et al.\textsuperscript{53}. As detailed previously\textsuperscript{18}, we have observed products that support the reactivity of a Criegee intermediate with a divalent 1,3-dipolar resonance form. This resonance form can be used to rationalize the cycloaddition reaction proposed in Scheme 3-6.

Although the stereo- and regiochemistry are not shown in Scheme 3-6, this type of cycloaddition is a concerted \textit{syn} addition\textsuperscript{54}. In this mechanism, the alkene moiety of oleic acid acts as a dipolarophile in accord with Huisgen’s description\textsuperscript{54}. The by-product
of this cycloaddition, 9-oxononanoic acid, is observed at 171 m/z; however, this same product is also observed under all ozonolysis conditions used in this work. A similar reaction with Criegee intermediate II would result in 9 or 10-oxooctadecanoic acid and nonanal, also one of the four classical products (Figure 3-2).

Polymer and oligomer formation in the oleic acid-ozone system may be significant in that the high molecular weight species can modify aerosol properties, including the ability to act as cloud condensation nuclei. Polymer and oligomer formation is also indicated in having a role in enhancing secondary organic aerosol growth\textsuperscript{12, 55, 56}. As of late many broad classes of atmospherically relevant organic compounds have been shown to have the propensity to polymerize or form oligomers in the laboratory, including in bag and chamber experiments. These classes of organic compounds include carbonyls\textsuperscript{10, 56, 57}, terpenes, including $\alpha$-pinene\textsuperscript{12, 55, 58, 59}, aromatic compounds\textsuperscript{11}, and cycloalkenes\textsuperscript{58}. As such, the role of these high molecular weight compounds in atmospheric processes merits further investigation. Our study, along with the work of others\textsuperscript{13, 14} show that polymerization may be possible with monounsaturated fatty acids such as oleic acid in the presence of ozone. Future effort will be placed on measurement in more realistic, mixed component particles, and on simulating atmospheric conditions to assess how significant a fraction of the overall particle mass these high molecular weigh compounds have under tropospheric conditions.
3.4. Conclusion

Herein we have provided the first direct experimental demonstration of polymerization in the heterogeneous ozonolysis of oleic acid particles. A mechanism has been proposed that is consistent with these observations made by PERCI-AMS. The presence of these polyanhydrides and previously reported secondary ozonides and cyclic geminal diperoxides further illustrates the capaciousness of this reactive medium that is the primary model for the reactions of aerosol phase monounsaturated fatty acids and oxidant trace gases. With the advent of increasing ozone, NOx, and other oxidants in the polluted troposphere, further consideration of the role of these oxygenates on the chemistry of the troposphere is needed.

3.5. References


4. The Heterogeneous Reaction of Particle-Phase Methyl Esters and Ozone
Elucidated by Photoelectron Resonance Capture Ionization: Direct Products of
Ozonolysis and Secondary Reactions Leading to the Formation of Ketones

4.1. Introduction

Accounting for the fate of organic carbon in tropospheric processing remains one of the most important problems in atmospheric chemistry today. Atmospheric chemical reactions are often heterogeneous, involving highly reactive trace gases, including, but not limited to OH•, SO2, NOx and ozone and aerosol particles, i.e., liquid- or solid-phase particulate dispersed in air. Analysis and modeling of these reactions lies in part with the complex secondary chemistry that often takes place, generating reactive chemical products that can remain in the condensed phase or be expelled from the particle into the gas phase. Although development of models that can provide insight into the chemical and physical processing of organic particulate phases is underway\textsuperscript{1-4}, efforts to obtain data necessary to improve existing models have been hampered by the lack of laboratory methods suitable to the detailed chemical study of complex, multicomponent organic particles. The study of simpler heterogeneous reaction systems is therefore a necessary first step to improve understanding of more realistic and environmentally relevant systems. In this respect, studies of the chemical reactions of two-component organic particles have been initiated\textsuperscript{5-7}. The focus of our research is to simulate and study
such multicomponent particles by a method developed in our laboratory, photoelectron resonance capture ionization (PERCI) aerosol mass spectrometry (AMS). Herein are reported results obtained by PERCI-AMS in elucidating the chemical products and mechanisms from the reaction of three-component organic particles with ozone.

Fatty acids are a major class of biogenic organics in the tropospheric particulate\textsuperscript{8-17}. As of late, 9-octadecenoic acid (oleic acid) has emerged as a model fatty acid for particle phase reactions with oxidizing gases, most notably ozone\textsuperscript{5, 6, 18-27}. Oleic acid appears to be a good choice for these studies because it has one double bond susceptible to ozonolysis, greatly simplifying the chemical description, and the ozonolysis of alkenes in traditional condensed phases is well characterized\textsuperscript{28, 29}. Oleic acid is also ubiquitous in both the pristine and polluted troposphere\textsuperscript{9, 11}. For example, levels of oleic acid on the order of 1 ng m\textsuperscript{-3} have been measured in the remote marine troposphere\textsuperscript{9}. Recently, we\textsuperscript{22, 24, 25} and others\textsuperscript{5, 6, 18-21, 23, 26, 27} have made advances in understanding the reactivity of particle phase oleic acid with ozone. In our work, we have directly measured products of secondary reactions of ozonolysis, including 1,2,4-trioxolanes (secondary ozonides) and cyclic geminal diperoxides. We have also directly observed formation of oligomers\textsuperscript{25} with weights up to 963 u via reactions of in situ-generated carbonyl oxides, commonly called Criegee intermediates, with the carboxyl groups of oleic acid. These oligomers were proposed to originate from $\alpha$-acyloxyalkyl hydroperoxides, which dehydrate to the corresponding polyanhydrides. Although there is evidence in the literature of hydroperoxides forming in the oleic acid-ozone system, our work and that of others\textsuperscript{18, 30} represents the first measurements of how first-generation
hydroperoxide products can participate as intermediates in the formation of high molecular weight oligomers. Advances in the chemical understanding of heterogeneous chemistry involving organic particles with oxidizing gases are largely facilitated by the soft ionization afforded by PERCI. This soft and tunable ionization method, when coupled with aerosol mass spectrometry, has proven to be a powerful tool for the investigation of chemical products of heterogeneous reactions on aerosol particles.

The work described herein is a description of the reaction of two multicomponent organic particles: oleic acid/methyl palmitate and methyl oleate/methyl linoleate/methyl linolenate with ozone. Described herein are the products of ozonolysis that are directly observed by PERCI-AMS and elucidation of a secondary reaction involving the cycloaddition of the unsaturated methyl esters (and corresponding fatty acids) with a Criegee intermediate. We propose that this secondary reaction leads to increases in the oxygen content of atmospheric particulate by formation of ketones in the processed particles. A mechanism for this reaction is proposed.

This work is significant in that it represents, to our knowledge, the direct observation of product evolution in a heterogeneous reaction system with a multicomponent particle phase, including products associated with secondary reactions. Furthermore, the existence of this recently observed oxidation pathway may impact aerosol chemistry models being developed insofar as changes in oxidative states of the organic compounds will affect the hygroscopicity of the reacted particles.
4.2. Experimental

4.2.1. Photoelectron Resonance Capture Ionization Aerosol Mass Spectrometer

A detailed description of the PERCI-AMS has been published previously\textsuperscript{24, 31}, however some modifications have been made. Briefly, aerosol particles are introduced into the mass spectrometer through a differentially pumped inlet and focused into a beam using an aerodynamic lens. A 220 $\mu$m diameter critical orifice at the entrance of the inlet keeps the aerosol sampling flow rate constant at 0.45 L/min. The ionization source consists of a low energy (sub-mJ) pulsed (10 Hz), tunable (235 – 300 nm) ultraviolet laser (Opotek Inc., Carlsbad, CA) focused gently onto the surface of a pure aluminum photocathode, generating a short (7 ns) burst of photoelectrons. For all results presented here, the laser wavelength was fixed at 270 nm. A vaporization probe is placed in close proximity ($\sim$ 1 cm) to the photocathode and intercepts the particle beam. Vaporization and analysis is done after collecting sampled aerosol on the vaporization probe (at room temperature) for a short time, $t_{\text{dep}}$. Mass analysis of the PERCI anions is achieved with a time-of-flight mass spectrometer (R. M. Jordan, Inc., Grass Valley, CA) operating in reflectron mode. Data is acquired at 1 GS/sec using a digital oscilloscope (WavePro 7000, LeCroy, Chestnut Ridge, NY). A trigger condition is set to save each laser shot in which an ion signal is detected within a given mass range (100-500 m/z in these experiments).
A significant change has been made to the vaporization source from that reported in previous publications\textsuperscript{24, 31}, incorporating temperature measurement and control. The new vaporization probe consists of a resistively heated Nichrome filament wrapped around a heat-conducting ceramic cylinder (radius \(\sim 2\) mm, length \(\sim 4\) mm) constructed from Resbond 919 electrically resistant ceramic adhesive (Cotronics Corp, Brooklyn, NY). Embedded into the heat-conducting ceramic is a type-k thermocouple junction. A CN8201 series Omega (Stamford, CT) temperature controller is used to monitor the temperature of the ceramic and to control the current applied to the filament. A maximum temperature of 400\(^\circ\)C is accessible with this source, well above the atmospheric pressure boiling points of the compounds studied. A temperature ramp from 40\(^\circ\)C to 385\(^\circ\)C over the course of 1 minute is used for these experiments, though in most cases the major components have been completely vaporized by the time the vaporizer reaches 200\(^\circ\)C, which takes approximately 20 seconds. There is some delay in transferring the heat from the filament to the ceramic, due to the larger thermal mass of the ceramic cylinder. Therefore, the temperature measured by the thermocouple embedded in the ceramic will lag the temperature of the filament, especially during a quick temperature ramp. The result is a quick burst in signal at the very beginning stages of the temperature ramp, presumably, as the deposited aerosol components that are in direct contact with the filament are vaporized first. The remaining deposited aerosol then vaporizes as the temperature of the ceramic cylinder increases.
4.2.2. Particle Generation and Flow Reactor

Fatty acid and ester particles are produced by nebulization (concentric pneumatic nebuliser, J.E. Meinhard Associates, Santa Ana, CA) of a dilute solution of the analyte in 15% ethanol in water. The particles are introduced to a flow reactor via a glass tube (0.32 cm I.D.), centered within a 2.54 cm ID flow reactor, which acts as the aerosol injector. Ozone is generated by passing USP medical air (Airgas Inc.) through an electric discharge ozonator (Model 8340, Mathesen). The concentration of ozone is determined spectrophotometrically by passing the air-ozone mixture through a 10.0 cm quartz cell (NSG Precision Cells, Inc., Farmingdale, NY) that is in line with a magnesium hallow cathode lamp and an echelle polychromator (ESA 3000, LLA Instruments GmbH, Berlin-Adlershof, Germany). Absorption of radiation at the 279.55 nm emission line of magnesium by ozone ($\sigma = 415.8 \times 10^{-20} \text{ cm}^2$) is used to determine the partial pressure of ozone flowing through the cell. The ozone is introduced into the flow reactor (2.54 cm I.D.) upstream of the aerosol injector. The flow of the gas is laminar (Re < 100) at one atmosphere total pressure within the flow reactor. The ozone exposure time for the particles is dictated by the position of the aerosol injector at a given flow rate of the particle and gas phases.

Table 4-1 gives the experimental details for each mass spectrum referenced in this work. The analytes used are methyl palmitate (MP), oleic acid (O), methyl oleate (MO), methyl linoleate (ML), and methyl linolenate (MLN). $P_{\text{ozone}}$ is the measured partial pressure of ozone in the flow reactor. The time of exposure of the particles to ozone is given as $t_{\text{ex}}$, while the collection time of particles on the vaporization probe is given as
Each mass spectrum referenced is an average of a series of single shot spectra collected during a particular collection and vaporization cycle. The number of spectra averaged and the total number of spectra saved for each experiment is given in Table 4-1. Also included is the temperature range over which the spectra contributing to the average were collected. Finally, some spectra were processed using an adjacent point average (10 points); it is noted in Table 4-1 where smoothing was applied.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Analyte</th>
<th>(P_{\text{zone}}) (atm)</th>
<th>(t_{\text{exp}}) (s)</th>
<th>(t_{\text{dep}}) (min)</th>
<th>Averaging</th>
<th>Temp Range (^\circ)C</th>
<th>Smoothing</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1</td>
<td>MP + O</td>
<td>(1.4 \times 10^{-4})</td>
<td>30</td>
<td>2</td>
<td>17/17</td>
<td>40-380</td>
<td>No</td>
</tr>
<tr>
<td>4-2</td>
<td>MO, ML, MLN</td>
<td>(1.0 \times 10^{-4})</td>
<td>46</td>
<td>5</td>
<td>9/33</td>
<td>40-175</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 4-1. Experimental conditions used in recording mass spectra. Mole fractions: MP: OL (0.53:0.47); MO: MLN: ML (0.33:0.34:0.33)

4.3. Discussion

4.3.1. Establishing Ionization Trends of Particle Phase Analytes

In a prior work\textsuperscript{31} we have shown that PERCI proceeds by both associative and dissociative electron attachment (AEA and DEA respectively) mechanisms. This trend
held with fatty acids and their methyl esters and is presumed to be mediated by the loss of
the hydrogen from the carboxyl group. Similarly, ionization of the methyl ester analogues
may proceed through loss of the methyl group, which, as discussed below, may lead to
some ambiguity in ion identification in a few cases. Herein we give an empirical
description of the PERCI of a model methyl ester: methyl palmitate (MP).

As detailed above, methyl palmitate was introduced into the flow reactor as a
mixed particle along with oleic acid (O). Oleic acid served as an internal standard for
calibration since its ozonized and non-reacted mass spectra and its PERCI response are
well established in our group\textsuperscript{22, 24, 25}. Methyl palmitate contains no alkene moiety,
eliminating potential complications in our initial attempts to describe ionization of a
methyl ester by PERCI or PERCI coupled with ozonolysis. Under the aforementioned
experimental conditions for assaying the effects of PERCI on MP/O mixed particles, a
medium intensity signal was observed at 269 m/z (Figure 4-1). We assign this signal,
which was absent from all prior studies with oleic acid, to the DEA ionization of MP, i.e.,
[MP-H]\textsuperscript{-}. Another peak of medium intensity is observed at 255 m/z, which we assign to
palmitate (P\textsuperscript{−}). The palmitate may be generated \textit{in situ} through thermal\textsuperscript{32} and/or optical\textsuperscript{33, 34} me-
chanisms, through the PERCI DEA process, or may be an impurity in the methyl
ester sample. While it may be interesting to determine the precise source(s) of acids in the
ester samples, the sources are not important to the ensuing discussions.
The general characterization of the ionization of esters, including methyl esters, by PERCI is being investigated in our laboratory currently. For the ensuing discussion involving reaction of a ternary particle composed of methyl esters, the observation of ionization by DEA and ions that are the carboxylates corresponding to their respective methyl esters is in good agreement with our preliminary results.

4.3.2. The Ozonolysis of Ternary Particles of Methyl Esters: Direct Observation of Primary Products

As described in an earlier work\textsuperscript{22}, ozonolysis of an unsaturated organic molecule, such as oleic acid, results in products associated with the decomposition of a 1,2,3-trioxolane (i.e., primary ozonides). These products are typically aldehydes or carboxylic acids under oxidative conditions\textsuperscript{35, 36} and for this work shall be referred to as
primary products. In this section, the primary products of ozonolysis of methyl esters and their corresponding carboxylic acids shall be described.

The ternary particles used for this study were composed of methyl oleate (MO), methyl linoleate (ML), and methyl linolenate (MLN). The molecular formulas for these methyl esters, their corresponding acids, and measured DEA ion signal masses are given in Table 4-2. The complete PERCI mass spectrum of a mixed particle of MO, ML, and MLN is shown in Figures 4-2a-d. In terms of anticipated ozonolysis products, methyl oleate should be the simplest of the three methyl esters assayed. Figure 4-2c shows a medium intensity signal at 295 m/z for the molecular ion of MO. This is in concert with the DEA observed in our preliminary studies with the binary MP/O system. The oleate, [O-H]-, is assigned to the signal at 281 m/z. Also evident in Figure 4-2 are other products associated with ozonolysis of MO including the ac-route products: 9-methoxy-9-oxononanoic acid (202 u), and nonanal (142 u); as well as bc-route products: methyl-9-oxononanoate (186 u) and nonanoic acid (158 u). It should be noted that the ion signal at 281 m/z can also arise from partial ozonolysis of MLN, as depicted in Scheme 4-1.
<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>FW (u)</th>
<th>m/z</th>
<th>Ion Signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>9,12,15-octadecatrienoic acid (linolenic acid)</td>
<td>CH$_3$CH$_2$CH=CHCH$_2$CH=CHCH$_2$CH=CH(CH$_2$)$_7$CO$_2$H</td>
<td>278</td>
<td>277</td>
<td>W</td>
</tr>
<tr>
<td>9,12-octadecadienoic acid (linoleic acid)</td>
<td>CH$_3$(CH$_2$)$_4$CH=CHCH$_2$CH=CH(CH$_2$)$_7$CO$_2$H</td>
<td>280</td>
<td>279</td>
<td>W</td>
</tr>
<tr>
<td>9-octadecenoic acid (oleic acid)</td>
<td>CH$_3$(CH$_2$)$_4$CH=CH(CH$_2$)$_7$CO$_2$H</td>
<td>282</td>
<td>281</td>
<td>W</td>
</tr>
<tr>
<td>Methyl 9,12,15-octadecatrienoate (methyl linolenate)</td>
<td>CH$_3$CH$_2$CH=CHCH$_2$CH=CHCH$_2$CH=CH(CH$_2$)$_7$CO$_2$CH$_3$</td>
<td>292</td>
<td>291</td>
<td>VW</td>
</tr>
<tr>
<td>Methyl 9,12-octadecadienoate (methyl linoleate)</td>
<td>CH$_3$(CH$_2$)$_4$CH=CHCH$_2$CH=CH(CH$_2$)$_7$CO$_2$CH$_3$</td>
<td>294</td>
<td>293</td>
<td>VW, B</td>
</tr>
<tr>
<td>Methyl 9-octadecenoic acid (methyl oleate)</td>
<td>CH$_3$(CH$_2$)$_4$CH=CH(CH$_2$)$_7$CO$_2$CH$_3$</td>
<td>296</td>
<td>295</td>
<td>VW</td>
</tr>
</tbody>
</table>

Table 4-2. Molecular formulas for methyl ester analytes. Key to assignments: VW-very weak, ≤ 1% \(I_{bp}\); W-weak, 1% < \(I_{bp}\) < 5%; M-medium, 5% < \(I_{bp}\) < 10%; S-strong, > 10% \(I_{bp}\); \(I_{bp}\) is the intensity of the base peak (73 m/z for propanoic acid); B-broad, > 2 Dalton base peak width.

Figure 4-2 a. See key at bottom of figure.
Figure 4-2b. See key at bottom of figure.

Figure 4-2c. See key at bottom of figure.
Figure 4-2. Complete PERCIMS mass spectrum for the mixed ternary particle MO/MLN/ML after reaction with O₃. The spectrum has been divided into 4 parts (a-d) to permit qualitative comparison of relative ion signal strengths. The peaks designated “a” and “b” in part b correspond to 143 and 155 m/z, respectively. The absolute signal intensity for the m/z 201 signal (parts (b) and (c) is 0.452. The signal-to-noise (1σ) of the m/z 297 peak is 13. Note the different scales of the ordinate. Experimental conditions given in Table 4-1.

The differences of ion intensity for a given decomposition route can be rationalized by considering several factors. Consider the stronger signal intensity of the 201 m/z ion, due to 9-methoxy-9-oxononanoic acid (HO₂C(CH₂)₇CO₂CH₃), compared to the other MO ac-route ion at 141 m/z (Figure 4-2b). Nonanal can be formed by only two oxidative cleavage routes in this ternary system, namely the ac-cleavage of MO and a similar cleavage of the O. On the other hand, there exist thirteen independent channels by which the 201 m/z ion can be formed. It should be noted that the 201 m/z ion, which can be formed by both partial and complete ozonolysis, can also be formed by channels from
MLN and ML in addition to MO. We have also observed in earlier studies of oleic acid that the ion signals are generally stronger for acids than for aldehydes under analogous experimental conditions, most likely due to a greater sensitivity of PERCI toward the acid moiety. In addition, the higher vapor pressure of nonanal may also contribute to its lower overall ion signal due to evaporative losses during particle collection onto the probe. These factors may explain, in part, the greater ion signal of 9-methoxy-9-oxononanoic acid compared to nonanal. Similar arguments with regard to the number of channels of ion formation, differences in PERCI sensitivity (i.e., ion formation efficiency) and vapor pressure can be used to explain many of the observed differences in ion intensity for a given cleavage route pair.
Scheme 4-1. Two pathways proposed for generation of the 281 m/z ion observed by PERCI-AMS: (a) a pathway directly from methyl oleate, (b) a pathway through methyl linolenate.

In terms of ozonolysis, methyl linoleate presents a more complicated substrate compared to methyl oleate due to its two double bonds. Methyl linoleate can be cleaved at just one double bond, i.e., partial ozonolysis, or be completely ozonized, undergoing oxidative cleavage at both double bonds. We observe ions associated with both extents of ozonolysis in the PERCI mass spectrum (Figure 4-2c-d), depending on total reaction time. The ML DEA molecular ion (293 m/z) appears as a very weak signal, while the ion signal at 291 m/z is assigned to MLN. The molecular ion formed by DEA of the corresponding linoleic acid (L) is clearly observed as a medium-weak intensity ion signal at 279 m/z (Figure 4-2c). In addition to the molecular ions of ML and L, there are only
three other DEA ions that can stem solely from these species by direct decomposition of their corresponding 1,2,3-trioxolanes. These ions are at 155, 139, and 99 m/z. All of the remaining ions can originate from MLN, MO, LN, and O. Notice the 155 m/z product, proposed to be the DEA ion of non-3-enoic acid, is much lower in intensity than neighboring ions at 153 and especially 157 m/z. The non-3-enoic acid can only arise from the bc-cleavage at the 9-position of ML and L, and is formed with one double bond remaining susceptible to ozonolysis. On the other hand, nonanoic acid (157 m/z) is not susceptible to further ozonolysis, which may explain, in part, its greater ion intensity. The case between the 153 m/z ion and the ion arising from non-3-enoic acid is not immediately clear: the former ion arises from nona-3,6-dienoic acid, which has two double bonds that are susceptible to ozonolysis. Notice that non-3-enoic acid can be further oxidized, forming primary products with masses at 116, 104, 100, and 88 u. A unique ion originating from ML/L is observed at 139 m/z and is likely the DEA product of non-3-enal, which can be formed only by the ac-route cleavage of the 9-position of ML or L. A summary of the remaining products, which could arise from ML/L along with other methyl esters and corresponding fatty acids are summarized in Table 4-3.
<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>FW (u)</th>
<th>m/z</th>
<th>Ion Signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propanal</td>
<td>CH₃CH₂CHO</td>
<td>58</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Malonaldehyde</td>
<td>HOCC₂H₃CHO</td>
<td>72</td>
<td>71</td>
<td>VW</td>
</tr>
<tr>
<td>Propanoic acid</td>
<td>CH₃CH₂CO₂H</td>
<td>74</td>
<td>73</td>
<td>Base</td>
</tr>
<tr>
<td>3-oxopropanoic acid</td>
<td>HO₂CCH₂CHO</td>
<td>88</td>
<td>87</td>
<td>VW</td>
</tr>
<tr>
<td>Hex-3-enal</td>
<td>CH₃C(H₂)₂CH=CHCH₂CHO</td>
<td>98</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Hexanal</td>
<td>CH₃C(H₂)₂CHO</td>
<td>100</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Malonic acid</td>
<td>HO₂CCH₂CO₂H</td>
<td>104</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Hex-3-enodial</td>
<td>HOCC₂H₃CH=CHCH₂CHO</td>
<td>112</td>
<td>111</td>
<td>W</td>
</tr>
<tr>
<td>Hex-3-enoic acid</td>
<td>CH₃C(H₂)₂CH=CHCH₂CO₂H</td>
<td>114</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>CH₃C(H₂)₃CO₂H</td>
<td>116</td>
<td>115</td>
<td>M, B</td>
</tr>
<tr>
<td>6-oxohex-3-enoic acid</td>
<td>HOCC₂H₃CH=CHCH₂CO₂H</td>
<td>128</td>
<td>127</td>
<td>W</td>
</tr>
<tr>
<td>Nona-3,6-dienal</td>
<td>CH₃C(H₂)₃CH=CHCH₂CHO</td>
<td>138</td>
<td>137</td>
<td>W</td>
</tr>
<tr>
<td>Non-3-enal</td>
<td>CH₃C(H₂)₃CH=CHCH₂CHO</td>
<td>140</td>
<td>139</td>
<td>W</td>
</tr>
<tr>
<td>Nonanal</td>
<td>CH₃C(H₂)₃CHO</td>
<td>142</td>
<td>141</td>
<td>M</td>
</tr>
<tr>
<td>Hex-3-enedioic acid</td>
<td>HO₂CCH₂CH=CHCH₂CO₂H</td>
<td>144</td>
<td>143</td>
<td>W</td>
</tr>
<tr>
<td>Nona-3,6-dienoic acid</td>
<td>CH₃C(H₂)₃CH=CHCH₂CH=CHCH₂CO₂H</td>
<td>154</td>
<td>153</td>
<td>S</td>
</tr>
<tr>
<td>Non-3-enoic acid</td>
<td>CH₃C(H₂)₃CH=CHCH₂CO₂H</td>
<td>156</td>
<td>155</td>
<td>W</td>
</tr>
<tr>
<td>Nonanoic acid</td>
<td>CH₃C(H₂)₃CO₂H</td>
<td>158</td>
<td>157</td>
<td>S</td>
</tr>
<tr>
<td>9-oxononanoic acid</td>
<td>HOCC₂H₃CO₂H</td>
<td>172</td>
<td>171</td>
<td>M</td>
</tr>
<tr>
<td>Methyl 9-oxononanoate</td>
<td>HOCC₂H₃CO₂H</td>
<td>186</td>
<td>185</td>
<td>M</td>
</tr>
<tr>
<td>Azelaic acid</td>
<td>HO₂C(H₂)₇CO₂H</td>
<td>188</td>
<td>187</td>
<td>M</td>
</tr>
<tr>
<td>9-methoxy-9-oxononanoic acid</td>
<td>HO₂C(CH₂)₇CO₂H₃</td>
<td>202</td>
<td>201</td>
<td>S</td>
</tr>
<tr>
<td>12-oxododec-9-enoic acid</td>
<td>HOCC₂H₇CH=CH(CH₂)₂CO₂H</td>
<td>212</td>
<td>211</td>
<td>W</td>
</tr>
<tr>
<td>Methyl 12-oxododec-9-enoate</td>
<td>HOCC₂H₇CH=CH(CH₂)₂CO₂H₃</td>
<td>226</td>
<td>225</td>
<td>W</td>
</tr>
<tr>
<td>Dodec-3-enedioic acid</td>
<td>HOCC₂H₇CH=CH(CH₂)₂CO₂H</td>
<td>228</td>
<td>227</td>
<td>W, B</td>
</tr>
<tr>
<td>12-methoxy-12-oxododec-3-enoic acid</td>
<td>HO₂C(CH₂)₇CH=CH(CH₂)₃CO₂H₃</td>
<td>242</td>
<td>241</td>
<td>W</td>
</tr>
<tr>
<td>15-oxopentadeca-9,12-dienoic acid</td>
<td>HOCC₂H₇CH=CH(CH₂)₇CO₂H₇</td>
<td>252</td>
<td>251</td>
<td>W, B</td>
</tr>
<tr>
<td>Methyl 15-oxopentadeca-9,12-dienoate</td>
<td>HOCC₂H₇CH=CH(CH₂)₇CO₂H₇</td>
<td>266</td>
<td>265</td>
<td>W</td>
</tr>
<tr>
<td>Pentadeca-3,6-dienedioic acid</td>
<td>HOCC₂H₇CH=CH(CH₂)₇CO₂H₇</td>
<td>268</td>
<td>267</td>
<td>W</td>
</tr>
<tr>
<td>15-methoxy-15-oxopentadeca-3,6-dienoic acid</td>
<td>HO₂C(CH₂)₇CH=CH(CH₂)₇CO₂H₇</td>
<td>282</td>
<td>281</td>
<td>W</td>
</tr>
</tbody>
</table>

Table 4-3. Predicted first-generation chemical products from the ozonolysis of MO, ML, MLN.

Methyl linolenate and linolenic acid, through possessing three double bonds susceptible to ozonolysis, potentially can form many more products than MO/O and ML/L. Nonetheless, ozonolysis of these compounds still forms products and ions by similar mechanisms described previously. Only a brief discussion of the most salient features of the ozonolysis of MLN/LN follows; however, a complete listing of all the primary products of ozonolysis is listed in Table 4-3.
The DEA molecular ions of MLN/LN are clearly evident in Figure 4-2c at 291 and 277 m/z, respectively. Products measured that are unique to MLN and LN are:

- Methyl 15-oxopentadeca-9,12-dienoate (265 m/z); pentadeca-3,6-dienedioic acid (267 m/z); 15-oxopentadeca-9,12-dienoic acid (251 m/z); nona-3,6-dienal (137 m/z); 6-oxohex-3-enoic acid (127 m/z); hex-3-enoic acid (113 m/z); hex-3-enedial (111 m/z); hex-3-enal (97 m/z); propanoic acid (73 m/z); and propanal (57 m/z). The higher m/z signals (251, 265, and 267) are also clearly evident.

Most of the lower m/z signals associated with ions arising solely from ozonolysis products of MLN/LN are less intense than their higher m/z congeners. The 137 m/z signal from nona-3,6-dienal is seen in Figure 4-2b as well as the signal at 127 m/z; formed from DEA of 6-oxohex-3-enoic acid. The 111 m/z ion assigned to hex-3-enedial is evident in Figure 4-2b, however, the expected ion signals at 97 m/z from hex-3-enal and the 57 m/z from propanal are absent, likely due to their rather high vapor pressure. Ions that can be formed from MLN/LN as well as ML/L and/or MO/O are summarized in Table 4-3.

There are thirty primary products of ozonolysis for this ternary system and six molecular ions for the methyl esters and corresponding fatty acids. Of these thirty-six products, 25 are clearly discernable from the baseline and have been assigned intensities ranging from weak (W) to strong (S) as defined in Tables 4-2 and 4-3. Peaks defined as very weak (VW) or broad (B), although assigned tentatively, were not considered in the total of 25. Five predicted peaks are not observed above the instrumental noise (57, 97, 99, 103 and 113 m/z); however, the 69 and 71 m/z signals may arise from
decarboxylation and DEA of hex-3-enoic acid (114 u) and hexanoic acid (116 u). The remaining anticipated primary products of ozonolysis are ambiguous, reported as very weak or broad, as summarized in Table 4-3.

4.3.3. The Dipolarophilic Reaction of Unsaturated Methyl Esters and In Situ-Generated Fatty Acids Leading to Ketone Formation

In a prior work$^{25}$ we described the formation of a molecular ion at 297 m/z in the oleic acid-ozone heterogeneous reaction system. We assigned this signal to 9 or 10-oxooctadecanoic acid. This was in accord with a model of cycloaddition-decomposition proposed by Katrib et al.$^{23}$ in an independent work. These workers described a cycloaddition of a Criegee intermediate (as a biradical) with the double bond of oleic acid, which, upon decomposition, lead to oxooctadecanoic acid. Our mechanism was similar except we showed it via a zwitterionic Criegee intermediate for reasons discussed in that work. Herein we present further evidence of the novel formation of a ketone, where the carbon-carbon double bond of an unsaturated methyl ester or fatty acid acts as a dipolarophile towards a Criegee intermediate. Furthermore, we provide evidence that polyunsaturated methyl esters and fatty acids may undergo multiple cycloaddition-decomposition cycles, thereby increasing the oxygen content of the organic particles that are exposed to ozone.

To test our hypothesis that the increase in m/z corresponding to 16 daltons stems from oxygenation about the carbon-carbon double bond, we assayed a mixed particle with equimolar concentrations of oleic acid and stearic acid (S) (PERCI mass spectrum not shown); the latter at 284 u being the saturated analogue of the former.
Unreacted oleic and stearic acids produced molecular ions of the same intensity (within 5%), indicating no significant measurement bias from the PERCI process. After ozonolysis of the equimolar O/S particles, a medium intensity peak was measured at 297 m/z ([O–H+Ox]-); however, only a very weak signal was observed at 299 m/z, which would be indicative of the [S-H+Ox]-. Note that in a prior publication we described a similar intensity peak in the oleic acid-ozone reaction system22, which we assigned to a secondary ozonide. Therefore, the absence of any enhancement in signal intensity at 299 m/z upon the addition of stearic acid supports the aforementioned hypothesis, that is, that carbonyl insertion occurs at the double bond. This is supported further by our studies with MP/O, in which the 297 m/z signal is clearly evident, while no significant signal is observed at 285 m/z or 271 m/z, which would correspond to oxygenation of methyl palmitate or palmitate, respectively (Figure 4-1). It should be noted that we have detected trace amounts of common fatty acids (L, LN, S, and P) in all oleic acid assayed to date. The unsaturated trace fatty acids (L and LN) could undergo a similar oxygenation to a ketone if our hypothesis is correct. Clearly evident in Figure 2d are ion signals at 297 m/z, [O-H+16]; 295 m/z, [L-H+16] and a lower intensity signal at 293 m/z, [LN-H+16]. Note that the ion signal at 293 m/z may also arise from the DEA ionization of methyl linoleate the ion signal at 295 m/z may arise from the methyl oleate. Therefore, these assignments are ambiguous. Recall that these ternary particles did not contain any significant amounts of the corresponding fatty acids upon generation, although as discussed above, traces of the acids could have been present, most likely through thermal degradation on the vaporization coil during heating32. Similarly, the 307 and 309 m/z are
assigned to oxygenated MLN and ML; however, the 311 m/z signal in accord with the oxygenation of MO is weak. Furthermore, we have observed the 311 m/z signal in prior studies of the oleic acid-ozone system\textsuperscript{22} and proposed that this ion arises from a 312 u anhydride formed in a reaction between 9-oxononanoic acid and a Criegee intermediate. Though the 311 m/z signal is weak, the presence of five of the other expected ions lends support to this model. We therefore believe that the unsaturated methyl esters, as well as the corresponding fatty acids, can undergo the cycloaddition-decomposition reactions with in situ-generated Criegee intermediates to generate ketones. The oxygenation products predicted by our mechanism below that are observed in this work for all methyl esters and their corresponding acids are summarized in Table 4-4.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>FW (u)</th>
<th>m/z</th>
<th>Ion Signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>LN + Ox</td>
<td>CH\textsubscript{3}CH\textsubscript{2}CO(CH\textsubscript{2})\textsubscript{2}CH=CHCH\textsubscript{2}CH=CH(CH\textsubscript{2})\textsubscript{7}CO\textsubscript{2}H</td>
<td>294</td>
<td>293</td>
<td>VW, B</td>
</tr>
<tr>
<td>L + Ox</td>
<td>CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{4}CO(CH\textsubscript{2})\textsubscript{2}CH=CH(CH\textsubscript{2})\textsubscript{7}CO\textsubscript{2}H</td>
<td>296</td>
<td>295</td>
<td>VW</td>
</tr>
<tr>
<td>O + Ox</td>
<td>CH\textsubscript{2}(CH\textsubscript{2})\textsubscript{4}CO(CH\textsubscript{2})\textsubscript{2}CO\textsubscript{2}H</td>
<td>298</td>
<td>297</td>
<td>W</td>
</tr>
<tr>
<td>MLN + Ox</td>
<td>CH\textsubscript{3}CH\textsubscript{2}CO(CH\textsubscript{2})\textsubscript{2}CH=CHCH\textsubscript{2}CH=CH(CH\textsubscript{2})\textsubscript{7}CO\textsubscript{2}H</td>
<td>308</td>
<td>307</td>
<td>VW</td>
</tr>
<tr>
<td>LN+2Ox</td>
<td>CH\textsubscript{3}CH\textsubscript{2}CO(CH\textsubscript{2})\textsubscript{2}CO(CH\textsubscript{2})\textsubscript{2}CH=CH(CH\textsubscript{2})\textsubscript{7}CO\textsubscript{2}H</td>
<td>310</td>
<td>309</td>
<td>W</td>
</tr>
<tr>
<td>ML + Ox</td>
<td>CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{4}CO(CH\textsubscript{2})\textsubscript{2}CO(CH\textsubscript{2})\textsubscript{2}CH=CH(CH\textsubscript{2})\textsubscript{7}CO\textsubscript{2}H</td>
<td>311</td>
<td>311</td>
<td>W, B</td>
</tr>
<tr>
<td>LN + 3Ox</td>
<td>CH\textsubscript{3}CH\textsubscript{2}CO(CH\textsubscript{2})\textsubscript{2}CO(CH\textsubscript{2})\textsubscript{2}CO(CH\textsubscript{2})\textsubscript{8}CO\textsubscript{2}H</td>
<td>326</td>
<td>325</td>
<td>VW</td>
</tr>
<tr>
<td>MLN + 2Ox</td>
<td>CH\textsubscript{3}CH\textsubscript{2}CO(CH\textsubscript{2})\textsubscript{2}CO(CH\textsubscript{2})\textsubscript{2}CO(CH\textsubscript{2})\textsubscript{8}CO\textsubscript{2}H</td>
<td>340</td>
<td>339</td>
<td>VW</td>
</tr>
</tbody>
</table>

Table 4-4. Abbreviated list of all novel ketones formed by the dipolarophilic reaction of an unsaturated methyl ester or fatty acid with a Criegee intermediate. Note: O denotes oxygen.

A mechanism leading to insertion of a ketone functionality into an unsaturated methyl ester is proposed. An example of this mechanism is presented in Scheme 4-2 using ML as a model substrate with a general Criegee intermediate (CI). The in situ-
generated Criegee intermediate is hypothesized to lose an oxygen atom after
decomposition of the cycloaddition product. As explained in a prior publication\textsuperscript{22},
Criegee intermediates generated \textit{in situ} probably rearrange to their corresponding
carboxylic acids, which are most likely the source of DEA ions generated \textit{via} PERCI. As
summarized in Table 4-3, nineteen acids (excluding O, L, and LN) have been assigned to
signals in our mass spectrum. All but three of these acids (9-oxononanoic acid, 172 u; 12-
oxododec-9-enoic acid, 212 u; 15-oxopentadec-9,12-dienoic acid, 252 u) can arise
through Criegee intermediates. This does not imply all of these acids arise \textit{solely} from
Criegee intermediates, however. A loss of 16 mass units due to deoxygenation of the
Criegee intermediates is in accord with our model. This would imply that the acids
observed that originate from Criegee intermediates would have an observed product ion
at seventeen mass units lower. Although there is evidence of fifteen of the sixteen
anticipated ions predicted by this model, cases can be made for contributions to these ion
signals by mechanisms independent from the one proposed in this work. Hence, the
presence of these ion signals neither supports nor disproves the proposed mechanism.
Their absence, on the other hand, would have disproved the proposed mechanism.

Polyunsaturated compounds, in theory, should be able to undergo multiple
cycles of cycloaddition-decomposition with Criegee intermediates. In the PERCI mass
spectrum of the ML/MLN/MO mixed particle (Figure 4-2d), a medium-intensity signal
measured at 325 m/z is tentatively assigned to the doubly oxygenated DEA ion of ML.
For LN, the doubly and triply oxygenated DEA signals appear at 309 and 325 m/z.
respectively. However, the 309 m/z could also arise, at least in part, from singly
oxygenated ML, and the 325 m/z from the doubly oxygenated ML. The medium intensity signal at 323 m/z and weak 339 m/z signal are tentatively assigned to the doubly and triply oxygenated MLN.

Scheme 4-2. Example of proposed mechanism of in situ ketone formation of an unsaturated methyl ester (ML) by an arbitrary Criegee Intermediate (CI). Note that for polyunsaturated methyl esters and fatty acids, multiple cycles of the proposed cycloaddition-decomposition are possible.
4.4. Conclusion

The impact of organic aerosols, pre- and post-atmospheric processing, on the atmosphere, climate and human health remain largely uncertain\textsuperscript{37, 38}. The physical and chemical properties of organic aerosols are driven by their chemical composition and, as such, our understanding of the chemical transformations of organic particles remains a priority. For example, increases in molecular oxygen content may increase their hygroscopicity\textsuperscript{39}, thereby impacting their ability to condensate water and form cloud droplets.

The work presented herein provides clear evidence of the evolution of the majority of products of a particle-gas phase heterogeneous reaction in which complex (i.e., greater than one component) particles were assayed. Of thirty-six primary products of ozonolysis (plus molecular ions) predicted for this ternary system, twenty-five were directly measured by PERCI-AMS. These products include both partial and complete ozonolysis products of the methyl esters and corresponding fatty acids.

In addition, a novel, secondary reaction was described, namely the cycloaddition of a Criegee intermediate with the double bond of an unsaturated methyl ester or fatty acid, which, upon decomposition, forms a new ketone. Multiple oxygenation cycles of polyunsaturates also is suggested from the PERCI mass spectra presented. Other secondary reactions, such as formation of secondary ozonides, as well as the chemical and physical kinetics will be described in a subsequent report.
4.5. References


5. The Ozonolysis of Primary Aliphatic Amines in Fine Particles

5.1. Introduction

Amines, including aliphatic amines, represent an important contributor to organic nitrogen in the atmosphere and stem from both anthropogenic and biogenic emissions. Animal husbandry is probably the most important anthropogenic emission source of amines into the troposphere\cite{1, 2} with Schade and Crutzen\cite{3} having estimated contributions up to $108 \pm 30$ and $24 \pm 15$ Gg N y$^{-1}$ for trimethylamine and methylamine to the atmosphere, respectively; albeit this is still 2-3 orders of magnitude lower than ammonia (23.3 Tg N y$^{-1}$). Agriculture\cite{4} and biomass burning\cite{5, 6} may also be important sources of amines to the troposphere. Other anthropogenic sources of amine or amine-derived nitrogen to the troposphere include vehicular emissions\cite{7}, industrial processes, and cooking\cite{8, 9}. In the marine troposphere organic amine nitrogen, including amino acids may enter the troposphere via a bubble bursting mechanism at the air-sea interface\cite{10}. Other biogenic sources of organic nitrogen, including amines, are addressed in the assessment provided by Neff and coworkers\cite{11}.

There is growing evidence that organic nitrogen, including amines and amine-derived compounds, may form a substantial fraction of the organic aerosol load as evidenced in recent field studies in remote\cite{4, 12}, urban\cite{7, 13-15}, and agricultural regions\cite{7, 13}, and in regions near extensive biomass burning\cite{5, 6, 14}. 

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Gas phase aliphatic amines may play a role in secondary aerosol formation via photooxidation and gas-to-particle conversion. Recent field observations have positively correlated episodic aerosol formation events with elevated concentrations of atmospheric amines. For example, Tan et al. have found in one episodic event of elevated PM$_{2.5}$ in an urban environment that organic amines were evident in all the particulate. Similarly, in remote boreal forest studies, Mäkelä and coworkers found a strong positive correlation between new particle formation events and the concentration of dimethylammonium (the ionic component of dimethylamine). This amine-derived species had more than 30-fold greater concentration during particle formation events as opposed to non-event concentrations for accumulation mode particles. In light of these recent findings, we believe that the role of amines and other forms of organic nitrogen in new particle formation events merits further investigation.

There is a need to develop a better model of the tropospheric chemical processing of amines and amine nitrogen, including understanding its incorporation into high molecular weight matter, such as humic like substances (i.e. HULIS) found in aerosols and hydrometeors. Answering questions about how nitrogen is incorporated into HULIS and its subsequent atmospheric processing is important in developing a better understanding of the aging of fine particulate matter in the troposphere. This processing may have implications on the cloud condensation nuclei ability of these particles, affecting global climate through indirect aerosol effects through the formation of more polar, water soluble compounds in aerosols. Moreover, developing a more comprehensive model of how amines and other classes of organic nitrogen are processed
in atmospheric particles will give us a better description of the deposition of nitrogen, and most broadly, better elucidate the role of organic nitrogen in the global nitrogen cycle –an area of high uncertainty and great concern\textsuperscript{11,19}.

Herein, we report on the heterogeneous ozonolysis of two long-chain, primary, aliphatic amines (octadecylamine, ODA; and hexadecylamine, HDA) in single component and mixed fine mode particles. These high molecular weight, low-volatility amines were chosen as model systems to minimize particle-to-gas phase partitioning, such that we could study their condensed phase reactivity in the aerosol. The second constituent in the two-component particles is either oleic acid (i.e. cis-9-octadecenoic acid, OL) or dioctyl sebacate (i.e. bis(2-ethylhexyl) sebacate, DOS). OL is a logical constituent for these particles in that it, and other fatty acids, are ubiquitous in the troposphere, forming coatings on continental aerosols\textsuperscript{20} and marine particulate matter\textsuperscript{21-23}, and are present in urban atmospheres as cooking\textsuperscript{8,24-26} and combustion emissions\textsuperscript{27}. Moreover, OL was chosen as a constituent for the mixed particles studies to investigate the reactivity of the products of ozonolysis of a common unsaturated fatty acid with the amines. As of late, a great deal of effort has gone into understanding the secondary chemistry resulting from the ozonolysis of unsaturated fatty acids\textsuperscript{28-33} and OL has emerged as a model compound for describing the heterogeneous ozonolysis of particulate rich in fatty acid content (for example, see review by Zahardis and Petrucci\textsuperscript{34}). The products of this secondary chemistry generally stem from the high reactivity of stabilized Criegee intermediates (SCI) and include high molecular weight, peroxidic oligomers\textsuperscript{29-33,35-37}. These types of products may have a role in the experimentally observed increase in
hygroscopicity and CCN activation of fine organic particles with ozonation. Conversely, DOS and similar high molecular weight esters (i.e. dioctyl adipate) are common constituents in studies of organic particles that are not a source of SCI and inert to ozone; hence, DOS serves as an excellent negative control for comparison to the studies of ozonized mixed particles of amines with OL.

Two specific goals of this work were to: a) identify chemical classes that may act as particle bound nitrogen sinks and that are representative of oxidatively stressed particulate matter; and b) compare the products formed from heterogeneous ozonolysis of particle bound alkyl amines with gas phase and solution chemistries. From this we hope to begin to better describe the atmospheric aging process of particles rich in organic nitrogen; identify chemical classes that may act potential molecular markers; and elucidate possible routes to nitrogen-rich HULIS formation.

5.2. Experimental Method

In this work we describe flow reactor based experiments employing photoelectron resonance capture ionization aerosol mass spectrometry (PERCI AMS), described in detail elsewhere. Briefly, molecular ionization by capture of low energy photoelectrons is a soft process that affords minimal fragmentation of the oxidized products with a high sensitivity for many oxygenated classes allowing for relatively straightforward mass spectral interpretation and subsequent product identification and mechanism development. Two modes of ionization have been described with near 0 eV
photoelectron attachment to organic molecules, namely associative (or non-dissociative) and dissociative electron attachment. In associative electron attachment a low energy photoelectron attaches to the molecule without any fragmentation of the analyte in the ionization process; whereas, dissociative electron attachment results in the loss of an atomic or molecular fragment concomitant to ionization of the analyte\textsuperscript{28, 36, 43-46}.

Polydisperse aerosols were generated using a glass, concentric pneumatic nebuliser (J. E. Meinhard Associates, Santa Ana, CA) and the solvent (100\% ethanol) was removed by passing the particle beam through a \textasciitilde 1 m columnar diffusion dryer packed with silica and activated charcoal. Although the activated charcoal has been shown to remove most of the ethanol from particles\textsuperscript{47} there may have been a small amount of residual ethanol left on the particles when ozonized. Aerosol number and mass size distributions were measured with a scanning mobility particle sizer (Model SMPS 3080, TSI Inc., Shoreview, MN) coupled with a condensation particle counter (Model 3010, TSI Inc., Shoreview, MN). In this work, both single and multicomponent particles were investigated composed of ODA (\textge 99 \%, Fluka, Seelze, Germany), HDA (\textge 99.0 \%, Fluka, Seelze, Germany), OL (\textapprox 99\%, Sigma-Aldrich, St. Louis, MO), azelaic acid (98\%, Sigma-Aldrich, St. Louis, MO), DOS (\textge 97\%, Fluka, Seelze, Germany). The geometric mean diameters and standard deviations of the particles were: OL (93.6 nm, 1.68), ODA (94.5 nm, 1.64), ODA + OL (98.6 nm, 1.59), HDA + OL (108 nm, 1.71), ODA + azelaic acid + DOS (103 nm, 1.66). Typical particle number densities were on the order of $10^7$ cm$^{-3}$. 1-nitrohexane (98\%, Sigma-Aldrich, St. Louis, MO) was used to investigate gas phase ionization of nitroalkanes.
Particles were introduced into a concentric glass flow reactor (2.54 cm i.d.) via a glass tube (3 mm i.d.) forming the movable aerosol injector. The flow rate in the reactor was held constant at 0.9 L min\(^{-1}\), such that positioning the aerosol injector from 1 to 51 cm from the end of the flow reactor resulted in reaction times from 0 to 17 s. Ozone was generated from USP Medical Air (UN1002, Airgas East, Williston, VT) or USP Oxygen (UN1072, Airgas East, Williston, VT) below and above 1x10\(^{-4}\) atm respectively, by high frequency corona discharge (OL80A/DLS, OzoneLab, Burton, BC, Canada) and quantified spectrophotometrically as described in an earlier report\(^{36}\). Particles entered the PERCI AMS through a 260 \(\mu\)m critical orifice giving a flow rate of 0.5 L min\(^{-1}\) and were introduced into the mass spectrometer through a differentially pumped particle inlet and focused into a beam using a series of aerodynamic lenses described elsewhere\(^{48-50}\). The focused particle beam was targeted onto a coiled Nichrome filament\(^{42}\) that could be heated resistively. For all experiments in this study the particle deposition time onto the filament was 2.5 minutes. After deposition, the filament temperature was ramped from room temperature to 400\(^{\circ}\)C over 10 seconds and then held at this temperature for 50 seconds. Anion mass spectra were recorded with a time-of-flight mass spectrometer (R. M. Jordan Inc., Grass Valley, CA) operating in reflectron mode.

Although the emphasis of this work was on investigating the heterogeneous processing of amines in particles, gas phase 1-nitrohexane was studied to better understand the fragmentation of aliphatic nitrocompounds by ionization with \(\sim 0\) eV photoelectrons. In these studies the analyte was introduced into the ionization region of
the mass spectrometer with a precision leak valve (model ULV-150, MDC Vacuum Products Corp., Hayward, CA).

5.3. Results

5.3.1 PERCI AMS ion profiles of the aliphatic amines, ODA and HDA, in single component particles and mixed particles of ODA (HDA) + DOS

The characteristic PERCI AMS profile for ozonized single-component particles consisting of primary, aliphatic amines was initially established under low and high ozone exposures (Figures 5-1a and b, respectively). Both ozonized ODA and HDA (not shown) are characterized by very strong \( \text{NO}_2^- \) \( (46 \text{ m/z}) \) and \( \text{NO}_3^- \) \( (62 \text{ m/z}) \) signals. A \( \text{NO}_2^- \) signal is evident with and without ozone exposure in single particles of the amines and all mixed particles containing the amines (i.e. OL + ODA (HDA), DOS + ODA (HDA)).
However, in all unexposed particles the NO\textsubscript{2}\textsuperscript{-} signal was weak, at about 10\% or less than for ozonized particles. The NO\textsubscript{2}\textsuperscript{-} signal is absent when all oxygen is removed from the system (i.e. both O\textsubscript{2} and O\textsubscript{3} are absent), namely when the nebuliser and carrier gases are N\textsubscript{2} or Ar. This implies that the volatilization of primary aliphatic amines in the presence of any oxygen may be a minor channel to NO\textsubscript{2} formation, compared to its direct formation via the oxidation of the amine by ozone. As shown in Scheme 5-1, the NO\textsubscript{2} most likely originates from progressive oxidation by ozone of the amine to the alkylhydroxylamine, then to the nitrosoalkane, and finally to the nitroalkane. This pathway is similar to the mechanism proposed for the ozonation of primary amines to nitro compounds on dry silica gel\textsuperscript{51} and in solution\textsuperscript{52, 53}.
Scheme 5-1. Pathways of direct oxidation and secondary reactivity with ozonized amines. ODA is shown as an example. The pathway labeled Direct Oxidation occurs with both single component particulate amines and in mixed particles with amine + OL. All products observed are underlined. The direct oxidation products are identical with ozonized HDA. The amides and imines that form in the HDA + OL mixed particles are similar in structure to those indicated, except 28 u lower in mass.

We do not detect any ions for the proposed nitroalkane end products of ozonized ODA or HDA. The NO$_2^-$ ion can arise from three sources: a) dissociative electron attachment of the nitroalkane, resulting in the formation of the NO$_2^-$ fragment ion; b) thermal decomposition of the nitroalkane$^{54}$ either in the flow reactor or c) in the volatilization process producing gas phase NO$_2$ with subsequent ionization via associative electron
attachment. To assay the viability of dissociative electron attachment forming NO$_2^-$, we investigated the ionization of gas-phase 1-nitrohexane at ~ 0 eV ionization energy (Figure 5-2). The base peak corresponding to NO$_2^-$ and a very weak signal arising from the dissociative electron attachment ion corresponding to the loss of hydrogen ([C$_6$H$_{12}$NO$_2$]$^-$, 130 m/z) are observed.

![PERCI mass spectrum of 1-nitrohexane introduced into the PERCI AMS as a gas. (p = 2 × 10$^{-5}$ atm, photoelectron energy was ~ 0 eV.](image)

Figure 5-2. PERCI mass spectrum of 1-nitrohexane introduced into the PERCI AMS as a gas. (p = 2 × 10$^{-5}$ atm, photoelectron energy was ~ 0 eV.)

We have made similar observations with other volatile nitroalkanes including nitrobutane and nitropropane, which further supports the viability of dissociative electron attachment forming NO$_2^-$ from nitroalkanes. Similarly, the formation of the NO$_2^-$ fragment with nitromethane$^{55, 56}$ and several nitrobenzene species$^{43, 55}$ has been reported with similar ionization energies. Thus it seems likely that nitroalkanes formed from progressive oxidation (Scheme 5-1) may be the source of NO$_2^-$ that occurs in the ionization process. It should also be noted that there is a weak NO$_3^-$ ion signal in the PERCI spectrum of 1-nitrohexane. This may be an experimental artifact arising from conversion of NO$_2$ to NO$_3$.
on the metal surfaces\textsuperscript{57} in the ionization region of the mass spectrometer or from a disproportionation reaction (Reaction 1)\textsuperscript{58}:

\[
\text{Reaction 1} \quad \text{NO}_2^- + \text{NO}_2 \rightarrow \text{NO}_3^- + \text{NO}. 
\]

We have evidence that there is decomposition of the particulate nitroalkanes both in the flow reactor and in the volatilization process. The former route to NO\textsubscript{2} formation is supported by the strong NO\textsubscript{2}\textsuperscript{-} signal evident from ozonized particles deposited on the Nichrome filament before heating the wire. Secondly, as shown in Figure 5-1, the NO\textsubscript{3}\textsuperscript{-} ion signal increases with ozone exposure, indicating that NO\textsubscript{2} is liberated from the nitroalkanes in the flow reactor at the particles’ surface or near surface and then oxidized according to the reaction\textsuperscript{59}:

\[
\text{Reaction 2} \quad \text{NO}_2 + \text{O}_3 \xrightarrow{\text{particle}} \text{NO}_3 + \text{O}_2. 
\]

In the ozonolysis of particle bound amines, the NO\textsubscript{3}\textsuperscript{-} ion signal was strong for all exposures, but increased in intensity with increasing ozone exposure. There are several possible pathways that we believe exist in forming this ion including: a) disproportionation (Reaction 1); b) oxidation of NO\textsubscript{2} by ozone (Reaction 2); and c) conversion of NO\textsubscript{2} to NO\textsubscript{3}\textsuperscript{-} via a surface reaction\textsuperscript{57} that occurs in the volatilization process. Reaction 2 is likely the most important pathway to NO\textsubscript{3}\textsuperscript{-} due to the concomitant increase in its ion signal intensity with increasing ozone exposure, as well as the very
weak ion signal for NO₃ in the gas phase studies that suggest Reaction 1 and surface processes are minor pathways. It should be noted that large molecular electron affinity (EA) of NO₂ (EA ~2.25-2.38 eV, see Ervin et al. and references therein) and NO₃ (EA = 3.92 eV, see Hirokawa et al. and references therein), may translate into large 0 eV electron capture cross sections, thereby increasing our sensitivity to these analytes; however, we cannot discount the possibility that there is a high conversion of the amines to the nitroalkanes at the particles surface upon ozone exposure.

There are also medium intensity ion signals in the ozonized ODA and HDA spectra at 125 and 226 m/z. These ion signals also increase with ozone exposure. We assign the 125 m/z ion signal to NO₃⁻•(HNO₃). This ion is the core ion of the series NO₃⁻•(HNO₃)ₙ(H₂O)ₘ, which is the most important negative ion family in the atmospheric at ground level. This ion may be formed from the following reaction sequence with the rapid ion-molecule association reaction being the final step:

\[
\begin{align*}
\text{Reaction 3a} & \quad 2 \text{NO}_2 + \text{H}_2\text{O} \xrightarrow{\text{particle}} \text{HONO} + \text{HNO}_3 \\
\text{Reaction 3b} & \quad \text{HNO}_3 + \text{H}_2\text{O} \xrightarrow{\text{particle}} \text{NO}_3^- + \text{H}_3\text{O}^+ \\
\text{Reaction 3c} & \quad \text{NO}_3^- + \text{HNO}_3 \xrightarrow{\text{particle}} \text{NO}_3^-\text{HNO}_3
\end{align*}
\]

Reaction 3a is the overall stoichiometry of the well-known surface reaction for the hydrolysis of NO₂ that generates both gas phase nitrous acid (HONO) and nitric acid. This entire reaction sequence could occur on either the surface of the particle and/or on the surface of the deposited particulate matter on the vaporization coil. The 125
m/z ion is observed evolving both before and during the volatilization process, indicating that formation of this ion is not exclusively a result of the thermal vaporization process used in generating the gas phase molecules requisite for ionization in PERCI AMS. This observation supports that at least a fraction of NO₅⁻•HNO₃ is formed on the surface of the particles.

An alternate route to NO₅⁻•HNO₃ is via N₂O₅, which could accumulate on the surface of the particle. This route follows Reaction 2 and results in the formation of nitric acid on the surface of the particle:

\[
\begin{align*}
\text{Reaction 4a} & \quad \text{NO}_2 + \text{NO}_3 \xrightarrow{\text{particle}} \text{N}_2\text{O}_5 \\
\text{Reaction 4b} & \quad \text{N}_2\text{O}_5 + \text{H}_2\text{O} \xrightarrow{\text{particle}} 2 \text{HNO}_3.
\end{align*}
\]

This reaction sequence is based on the premise that a fraction of NO₂ is generated at or near the surface of the particle as a result of decomposition of the nitroalkane that formed by the mechanism of progressive oxidation. The NO₂ then reacts with ozone to give NO₃⁻. The NO₃ subsequently reacts with NO₂ to give N₂O₅, which hydrolyzes in the presence of water, yielding nitric acid. This last step (i.e. Reaction 4b) is akin to the hydrolysis of N₂O₅ that has been described previously on aerosols. As shown in Figure 2, the reactant water in Reaction 4b forms on the surface of the particle via the oxidation of the intermediate alkylhydroxylamine to the nitrosoalkane. The resulting nitric acid could then proceed by Reaction 3c to give NO₅⁻•HNO₃.
The 226 m/z ion does not correspond with any anion cluster in the NO$_3^-$•(HNO$_3$)$_m$(H$_2$O)$_n$ series, and to the best of our knowledge, it is not a commonly observed ion containing any combination of H, N, and O$^7$. This ion is observed not only in the ozonolysis of ODA and HDA, but also for ozonized octylamine (129 u) and lysine (146 u), indicating that it is not an ion directly arising from the fragmentation of the amine (or amino acid) or their corresponding nitrocompounds. We tentatively assign this ion signal to the cluster NO$_2^-$•(HNO$_3$)$_2$(H$_2$O)$_3$. Although, to our knowledge, this ion has not been observed, we hypothesize that it could originate from HNO$_3$•NO$_2$. This species has recently been detected in the attenuated total reflectance FTIR studies of the heterogeneous hydrolysis of NO$_2$.$^7$ A small ion signal at 163 m/z is also evident in the PERCI spectrum that becomes more intense with increasing ozone exposure. We tentatively assign this to another member of this proposed ion series, NO$_2$•(HNO$_3$)(H$_2$O)$_3$. Even at high ozone exposures, the 163 m/z ion signal is relatively weak compared to the four signals discussed previously (i.e. 46, 62, 125, and 226 m/z) for the ozonized single-component amine particles. For simplicity, in the remainder of this work we will refer to the 4 strongest ions of the ozonized single-component amine particles as the ‘characteristic ions of the amine’.

Nitrite and nitrate ions were measured in all single-component particles of ODA and HDA and in mixed particles containing the amines and well as DOS as the second component. The DOS + amine PERCI spectrum is relatively simple with three of the ions having been determined to be unique to the ester: the dissociative electron attachment ion ([DOS-H]) at 425 m/z, and two fragments 295 and 313 m/z. These ions probably arise
from the fragmentation of the ester linkage\(^{45}\), with 313 m/z assigned to \([\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{OCO}(\text{CH}_2)_8\text{COO}]^–\). The 295 m/z ion is tentatively assigned to \([\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{OCO}(\text{CH}_2)_6\text{CH}═\text{CHCO}]^–\) or similar dehydration product of the 313 m/z fragment. There was no measurable difference in the PERCI mass spectrum of pure DOS particles upon ozonolysis. The four characteristic ions of the amine were also observed for both ODA and HDA upon ozonolysis of the mixed particles containing DOS. The PERCI mass spectrum of ODA (or HDA) + OL, on the other hand, is far more complex.

5.3.2 Ozonolysis of ODA (HDA) in Mixed Particulate Matter – Overview

DOS and other related high molecular weight esters\(^{29,41}\) employed in studies of heterogeneous ozonolysis are used often as controls because they are not a source of Criegee intermediates (CI). The reactivity of SCI with ODA and HDA was a key feature in the oxidative processing of these mixed particles, especially in the formation of high molecular weight compounds. Ozone concentrations were varied from the same order of magnitude as typical summertime maximum daily concentrations in a suburban-urban troposphere (100 – 400 ppb i.e. 1– 4 x 10\(^{-7}\) atm)\(^{72}\) to very high concentrations: up to ~ 10\(^{-3}\) atm. Assaying the effects of high ozone concentrations on mixed particles helped in elucidating the mechanisms of oxidation. Secondarily, the products formed under high oxidative stress may be similar to products formed when particulate matter with high
amine and lipid content (i.e. meat cooking aerosols) is subjected to both thermal stress and enhanced ozone levels associated with the urban troposphere.

For conciseness, the ensuing discussion places emphasis on comparing the low ozone exposure regime (which we define as $10^{-6} – 10^{-7}$ atm ozone for ~17 s) to the very high ozone exposure regime ($\geq 10^{-3}$ atm for ~17 s).

5.3.3 Ozonolysis of ODA (HDA) + OL in Mixed Particles: Products Assignments for Low Ozone Exposure

Figures 5-3a, b compare PERCI mass spectra for the ozonolysis of mixed ODA/OL particles at $3 \times 10^{-7}$ atm and $2 \times 10^{-3}$ atm ozone, respectively, for a 17 s reaction time. Of the four expected lower molecular weight products of the heterogeneous ozonolysis of OL$_{34}$ (i.e., azelaic acid (188 u), 9-oxononanoic acid (172 u), nonanoic acid (158 u), and nonanal (142 u)), only azelaic acid (187 m/z) is observed for the mixed particles (ODA (HDA) + OL), at very low exposure. On the other hand, all 4 characteristic ions expected from reaction of the aliphatic amine (46, 62, 125, and 226 m/z), as well as the minor ion at 163 m/z are observed.
Figure 5-3. PERCI mass spectrum of ozonized mixed particles of ODA + OL at $p_{O_3} = a) 3 \times 10^{-7}$ atm and b) $2 \times 10^{-3}$ atm. Reaction time was 17 s, mole fractions ($\chi$), were $\chi_{ODA} = 0.41$ and $\chi_{OL} = 0.59$. 
At ozone exposures of $\sim 3 \times 10^{-7}$ atm (17 s) and higher in the ODA + OL system, we also observe ions at 422 and 438 m/z. The 438 m/z ion is assigned to the amide that may be formed by several pathways, including reaction of the SCI-I (c.f. Scheme 5-1) with ODA. The 422 m/z ion could arise from a 423 u product that is either an amide or an imine (i.e. Schiff base). The amide could be formed from ODA and 9-oxononanoic acid, with the amine reacting at the carboxyl position. The imine (i.e. Schiff base), 9-(octadecylimino)nonanoic acid, could be a product of the reaction of ODA with the aldehyde functionality of 9-oxononanoic acid. This ion is nominally one mass unit lower than the mass of the proposed ion indicating dissociative electron attachment ionization via the loss of hydrogen. These assignments are supported by ion signals measured at 394 and 410 m/z in the HDA + OL mixed particles ($p_{O3} = 3 \times 10^{-7}$ atm and 17 s reaction time). These higher molecular weight signals are assigned to the amides and imine corresponding with reaction of HDA with 9-oxononanoic acid and SCI-I respectively. These ions are not observed at lower concentrations of ozone in the ODA (HDA) + OL reaction system. These ion signals are also not observed under any conditions of ozone exposure for ODA or HDA in DOS. It should be noted that we do not observe any dissociative electron attachment ion for the amides that could be the product of the reaction of the 158 u SCI (SCI-2, i.e. OOCH(CH$_2$)$_7$CH$_3$) with ODA or HDA. These amides would have an alkyl end, unlike the amides arising from the reaction of SCI-1 which have a carboxyl group functionality. It is likely that SCI-2 does form amides with these amines, but they are not ionized to any significant extent with $\sim 0$ eV electrons, as is the case with all organic acids$^{28, 36, 42, 44}$ investigated to date. The high
molecular weight, nitrogen-containing products measured and their corresponding assignments are summarized in Table 5-1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Product</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₃(CH₂)₁₇NHCO(CH₂)₇CHO</td>
<td>422 m/z, Secondary amide, ODA + OX -H₂O</td>
</tr>
<tr>
<td>2</td>
<td>CH₃(CH₂)₁₇N=CH(CH₂)₇CO₂H</td>
<td>422 m/z, imine, ODA + OX -H₂O</td>
</tr>
<tr>
<td>3</td>
<td>CH₃(CH₂)₁₇NHCO(CH₂)₇CO₂H</td>
<td>438 m/z, secondary amide, ODA + SCI⁻¹ -H₂O</td>
</tr>
<tr>
<td>4</td>
<td>CH₃(CH₂)₁₇N(CO(CH₂)₇CHO)₂</td>
<td>576 m/z, tertiary amide, ODA + 2 OX -2 H₂O</td>
</tr>
<tr>
<td>5</td>
<td>CH₃(CH₂)₁₇N(CO(CH₂)₇CHO₂)</td>
<td>592 m/z tertiary amide, ODA + OX + SCI⁻¹ - 2 H₂O</td>
</tr>
<tr>
<td>6</td>
<td>CH₃(CH₂)₁₇N(CO(CH₂)₇CO₂H)₂</td>
<td>608 m/z tertiary amide, ODA + 2 SCI⁻¹ - 2 H₂O</td>
</tr>
</tbody>
</table>

Table 5-1. High molecular weight, nitrogen containing products formed in the heterogeneous ozonolysis of mixed ODA/OL particles and assignments. The corresponding ions, with masses 28 u lower were observed in the HDA/OL system.

5.3.4. Ozonolysis of ODA (HDA) + OL in Mixed Particles: Products Assignments for High Ozone Exposure

The mass spectrum of products arising from heterogeneous reaction ODA(HDA) + OL aerosols with ~2 x 10⁻³ atm ozone at ~ 17 s reaction time (Figure 5-3b) shows the four characteristic ions of the aliphatic amine (i.e. 46, 62, 125, and 226 m/z) in addition to two distinct regions of high molecular weight products, mainly the dissociative electron attachment ions of secondary and tertiary amides formed via the secondary reactions of ozonolysis. The four classical products of OL ozonolysis are also
evident in both the ODA and HDA mixed particles. Interestingly, the OL molecular ion at 281 m/z is one of the strongest ion signals in the PERCI mass spectrum for the ozonolysis of ODA + OL aerosols (Figure 5-3), but only a very weak signal in the HDA + OL system at this same exposure (not shown). Under identical exposure conditions, the OL molecular ion was not observed in the reaction of pure OL particles. Moreover, for the pure OL particles, no OL molecular ion was observed for any ozone concentration above 1x 10^-4 atm ozone for ~ 17 s reaction time. We believe these unanticipated effects (i.e. the retention of OL in the ODA + OL reaction system at this very high ozone exposure) originate from surface or near surface reactions that produce high molecular weight secondary and tertiary amides. These surface active species, in turn, may impede the diffusion of ozone into the particle and limit the diffusion of OL to the surface, thereby effectively shutting down the ozonolysis of OL.

5.3.5. A Mechanistic Account for the Formation of the Observed Products in the Ozonized Mixed Particles

A detailed account of the heterogeneous ozonolysis of OL has recently been published\textsuperscript{34} and many mechanistic depictions are available in the literature\textsuperscript{28, 29, 31, 32, 73, 74}. The three main steps of ozonolysis of oleic acid are in accord with established solution phase chemistry:

Step 1) formation of the primary ozonide (i.e. 1, 2, 3-trioxolane)
Step 2) decomposition of the primary ozonides to aldehydes and excited Criegee intermediates, which in solution rapidly stabilize to SCI

Step 3) recombination of the SCI and aldehyde to form secondary ozonides (and other reactions including: intermolecular reactions to form diperoxides, or reactions with acids e.g. OL, to give \( \alpha \)-acyloxyalkyl hydroperoxides)

There exists considerable debate concerning the formation of azelaic acid and nonanoic acid and their relationship with SCI-1 and SCI-2\(^{34}\). It has been suggested that these two acids are formed from isomerization of SCI-1 and SCI-2 (i.e. \( \text{OOCH(CH}_2\text{)}_7\text{CO}_2\text{H} \) and \( \text{OOCH(CH}_2\text{)}_7\text{CH}_3 \))\(^{28, 29, 32, 75}\) or, conversely, form as decomposition products of the secondary ozonides and other peroxides as higher generation reaction products\(^{76, 77}\). Recent mass spectral evidence\(^{31}\) suggests that fragmentation occurring in the ionization process of high molecular weight peroxides may also contribute to the evolution of ions corresponding to these acids. A more extensive discussion of the formation of these acids as well and other mechanistic features of this reaction system are beyond the scope of this report and have been covered elsewhere\(^{34}\).

The amide 9-(octadecylamino)-9-oxononanoic acid (439 u, 438 m/z) may be formed by several different routes in the ozonolysis of ODA + OL. Route 1 is the well-established route via acylation of an amine by a carboxylic acid (i.e. azelaic acid)\(^{78}\), which we believe to be a minor pathway in the formation of amides in these
heterogeneous reaction systems. *Route 2* involves reaction of the amine (ODA) with SCI-1 (Scheme 5-2a), while *Route 3* may result in amide formation via reaction of ODA with a secondary ozonide (Scheme 5-2b). Similar routes exist for the formation of 9-(hexadecylamino)-9-oxononanoic acid (411 u, 410 m/z) in the HDA + OL reaction system.

Scheme 5-2. Proposed mechanisms for observed amide formation via reactions of amines with products of ozonolysis of OL: a) ODA with an SCI and b) ODA and a secondary ozonide. The Criegee intermediate shown in (a) is SCI-1. Similar reactions for HDA are discussed in text.
We tested the relative importance of Routes 2 and 3 by preparing mixed particles with a very high concentration of azelaic acid. These mixed particles contained the inert matrix DOS, which like other esters does not undergo ozonolysis or react with SC1\textsuperscript{29, 41}. Figure 5-4 compares the evolution of the 438 m/z amide between the azelaic acid + ODA + DOS and ODA + OL heterogeneous reaction systems, at four ozone concentrations.

![Graph showing ion signal vs. ozone concentration](image)

Figure 5-4. Formation of a (■) secondary amide (438 m/z) and (▲) SCI-1 (187 m/z) in ODA + OL in mixed particles (\( \chi_{\text{az}} = 0.59, \chi_{\text{oda}} = 0.41 \)) compared to the formation of (□) secondary amide (438 m/z) in azelaic acid (AZ) + ODA + DOS mixed particles (\( \chi_{\text{az}} = 0.22, \chi_{\text{oda}} = 0.24, \chi_{\text{dos}} = 0.54 \)) with no possible concurrent formation of SCI-1 in particle. Error bars indicate one standard deviation.

The 438 m/z ion was either not observed or was a very weak signal in the azelaic acid + ODA + DOS mixed particles under all exposure conditions. Further, no other ion signals...
corresponding to amides were observed in the azelaic acid + ODA + DOS heterogeneous reaction system. On the other hand, the 438 m/z amide was produced in significant amounts in the ODA + OL reaction system (Figure 5-4) and was directly proportional to the ion signal for azelaic acid generated in situ to the ODA/OL particle. The direct proportionality of amide formation with azelaic acid does not contradict the aforementioned result because the azelaic acid signal we measure is directly proportional to the in situ generated SCI-1 and likely directly proportional as well with the secondary ozonides in the system that can decompose to the acid. Our results indicate it is the reactivity of these chemical classes (i.e. SCI and secondary ozonides) with the amines that constitute the main routes to amides; however, with the extant data there is no way to estimate the relative importance of Route 2 vs. 3.

The observation that classic acylation route to the amide is a minor pathway suggests that the 422 (394) m/z product observed in the ODA (HDA) + OL reaction system arises from the reaction of amine with the aldehyde moiety of 9-oxononanoic acid, rather than the carboxyl group, i.e. the 422 (394) m/z products are most likely imines. The formation of imine products from the reaction of aldehydes and ketones with primary amines has been shown to have a rapid rate of reaction\(^79, 80\). For example, the imine forming reaction between methylamine and \(n\)-propylamine with isobutyraldehyde are given by second order rate constants (35 °C) of 53 and 50 M\(^{-1}\)s\(^{-1}\), respectively\(^80\). It should be noted that these kinetic studies were done in aqueous solutions\(^79, 80\), so caution should be taken in directly comparing the results of these studies with our particle-based flow reactor experiments, especially since these particles were initially anhydrous with
water formed by the in situ oxidative processing of the amines with ozone (see Scheme 5-1).

### 5.3.6. The Formation of a Solid or Viscous Surface Layer

The OL ion signal was measured for three types of ozonized particles as a function of ozone exposure: (neat) OL, ODA + OL, and HDA + OL (Figure 5-5). The OL ion signal in neat particles and mixed particles of HDA + OL follows an exponential decay at low ozone exposures. Neither of these particles shows a measurable OL signal at ozone exposures above $1 \times 10^{-4}$ atm at 17 s reaction time. In the ODA + OL reaction system, on the other hand, OL decays exponentially initially up to an ozone exposure of $1 \times 10^{-4}$ atm but then re-emerges at very high exposures ($\geq 6 \times 10^{-4}$ atm for 17 s reaction).

![Figure 5-5](image_url)

Figure 5-5. Comparison of OL decay for three particle types: (•) neat OL particles, (▲) ODA/OL mixed particles, and (□) HDA/OL mixed particles. Mole fractions, $\chi$, were $\chi_{\text{ODA/HDA}} = 0.41$ and $\chi_{\text{OL}} = 0.59$. 

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This suggests that at a critical level of ozone exposure, the particles develop a solid or highly viscous liquid surface layer that impedes the diffusion of ozone into the particle. Similar effects have been observed in the formation of solid surface layers with ozonized myristic acid + OL particles. Figure 5-6 compares the PERCI ion signal of OL (281 m/z) to the integrated ion signal of 5 high molecular weight imine and amide products (422, 438, 576, 592 and 608 m/z) and the integrated ion intensity of the 438 m/z amide.

![Figure 5-6. OL decay and the formation of amides and imine in ozonized mixed particles of ODA/OL.](image)

The ion intensity of the 438 m/z amide increases rapidly for ozone exposures in the range 0 to 1 x 10^{-4} atm and 17 s reaction time. Furthermore, no appreciable increase in intensity is measured at higher exposures. In comparison, the 422 m/z amide/imine and the three high molecular weight tertiary amides show less rapid initial increase in their ion intensity with a linear, generally monotonic, increase in intensity at exposures above 1 x 10^{-3} atm.
$10^{-4}$ atm O$_3$. The total amide/imine ion intensity rapidly rises for a 17 s reaction with $0 - 1 \times 10^{-4}$ atm O$_3$. At higher exposures, a linear, monotonic increase is observed, with the exception of the $1 \times 10^{-3}$ atm O$_3$ exposure, where there is a slight decrease in the PERCI ion intensity. From these data, we cannot definitively assign any particular imine or amide with the formation of a solid or viscous liquid layer that impedes the diffusion of ozone into the particle, although it appears that the best correlation is between the total amide/imine content and the formation of this layer.

5.4. Conclusions and Implications

The experiments described in this work have lead to several significant observations for the ozonolysis of particle bound amines.

1) Our observation of a strong ion signal corresponding to nitrogen dioxide indicates nitroalkanes are generated from primary aliphatic particulate amines by the mechanism of progressive oxidation$^{51-53}$. This is in accord with the ozonolysis of amines in solution$^{52, 53}$ and on dried surfaces$^{51}$ rather than in the gas phase$^{7, 16, 82}$, where large yields of aldehydes would be anticipated$^{82}$. We do not observe any aldehyde or other oxygenate signal in the ozonolysis of single component particles of amines under any conditions of ozone exposure. This probably stems from the stabilization of either the amine oxide or alkylhydroxylamine (Scheme 5-1) early in the reaction sequence in the ozonolysis of the particulate amines.
Stabilization would favor the formation of the nitrosamine, which is subsequently oxidized to the nitroalkane. This is quite different than in the gas phase, where the excited amine oxide or alkylhydroxylamine intermediate fragments\textsuperscript{82}, leading to a host of products including nitroalkanes, aldehydes, and imines.

2) The ozonolysis of particles of primary, aliphatic amines may represent a source of NO\textsubscript{2}, NO\textsubscript{3} and nitric acid ion clusters, even at ozone concentrations that correspond to a polluted suburban-urban troposphere\textsuperscript{72}. The experimental data reported herein suggests that progressive oxidation of amines leads to NO\textsubscript{2} formation, with subsequent formation NO\textsubscript{3} through progressive oxidation (as described above) and finally nitric acid ion clusters. As described in Reactions 4a-b, an alternative pathway to nitric acid, and subsequently the nitric acid ion cluster, is via the reaction of NO\textsubscript{2} and NO\textsubscript{3} to N\textsubscript{2}O\textsubscript{5}, followed by hydrolysis. This may help explain, in part, the mechanism by which organic nitrogen in fog water and aerosols acts as a source of NO\textsubscript{x} and NO\textsubscript{3} during exposure to ozone\textsuperscript{83}. Future emphasis will be placed on quantification of NO\textsubscript{2}, NO\textsubscript{3}, and the nitric acid ion clusters via PERCI for the ozonolysis of a wider array of particle bound organic species that contain amine nitrogen. This is inherently challenging because many of the anticipated products (i.e. NO\textsubscript{2} and NO\textsubscript{3}) do not have well-established capture cross-sections for very low energy photoelectrons. We will also investigate the effects of relative humidity on the formation of nitric acid ion clusters.
The experiments described in this work have lead to several significant observations in the heterogeneous ozonolysis of mixed particles containing amines:

1) Secondary and tertiary amides and possibly imines are potentially important reaction products of the heterogeneous ozonolysis of aliphatic primary amines in particles, when SCI can be generated in situ to these mediums. These products are evident even at relatively low ozone exposures for relatively short reaction times. This implies that in regions where there is a high atmospheric input of amines (i.e. near animal husbandry operations), there may be an enhanced incorporation of these nitrogen-containing species into particles. SCI have been shown to form and react near or on the surface of ozonized OL particles. When gas-phase amines partition to the surface of an ozonized particle that contains SCI and/or secondary ozonides, they may react via Reaction 2 and/or 3 to form the lower volatility amides. This is evidenced by our observation of these high molecular weight products even at low ozone exposures (c.f. Figure 5-1a). These reactions represent new pathways by which amine nitrogen may be converted to lower volatility particle bound nitrogen. They may also help explain the mechanism of forming nitrogen enriched HULIS and may be important in the atmospheric aging of organic aerosols. Moreover, amides, compared to other acylation products such as esters, are relatively stable to hydrolysis, resulting in the potentially long atmospheric lifetime of these nitrogen containing species in
particles. The viability of gas-to-particle conversions of amine nitrogen via these mechanisms will be the focal point of upcoming environmental chamber experiments in our laboratory where we will examine the effects of prolonged ozone exposure (hours to days) of more common atmospheric amines (i.e. ethyl amines) in the presence of unsaturated acids at ozone levels in accord with a polluted suburban-urban troposphere.

2) Although amide production is in accord with well-established solution acylation reactions (i.e., between the carboxylic acids and the amine)\textsuperscript{78}, our data implies that the major pathway(s) in ozonized particles of ODA (HDA) + OL is through the reaction of SCI and/or secondary ozonides with the amine. This may have ramifications to source apportionment where it has been suggested that amides can be utilized as molecular markers\textsuperscript{14} for biomass burning events, since they can be generated by standard (i.e. Route 1) acylation under pyrolysis. Although we agree with the importance of this route of amide formation under biomass burning conditions, we need to establish the viability of the role of secondary chemistry of ozonolysis in sequestering amine nitrogen into particulate matter via amide formation (i.e. Routes 2 and 3). These routes, if important competing pathways to amide formation through acylation would indicate that amides may also be molecular markers for regions that have concurrent high levels of ozone and amine input, i.e. animal husbandry operations near polluted suburban-urban environments.
3) There is evidence of solid surface or highly viscous liquid layer formation in ODA + OL at high ozone exposures. This may impede the diffusion of ozone into the particle causing retention of OL at these very high exposures, where it would be totally consumed in single component particles of OL. This observation and similar ones by others in fatty acid rich particulate, along with the retention of OL even at high exposures, may help elucidate the disparity that exists between the lifetime of OL measured in the field vs. in the laboratory. The formation of high molecular weight amides is likely to occur in meat-cooking aerosols that are rich in both fatty acids and amines and that are formed under conditions of high temperature (facilitating Route 1 amide formation). Amide formation is especially significant when generated in a polluted, ozone rich troposphere (facilitating amide formation via Routes 2 and 3). The prolonged lifetime of OL in real meat cooking aerosols vs. single-component particulate OL matter has also been demonstrated experimentally. Although we only observe the solid surface or highly viscous liquid layer formation in the OL + ODA reaction system under conditions of very high ozone exposure (1 x 10^-4 atm O3, 17 s reaction time), we need to investigate the effects of prolonged exposure of particles to lower levels of ozone (~ 10^-7 atm O3) with experiments in environmental chambers. Although not explored in this work, other condensed phase thermo-chemical effects that may cause a prolonged lifetime of OL and other unsaturated components of real
atmospheric aerosols, such as gel or semisolid formation, or Ostwald ripening in amide enriched aerosols needs to be explored as well.

5.5. References


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6. Conclusions and Future Directions

6.1. Conclusions

PERCI AMS has been shown to have utility in the analysis of the oxidative processing of fatty acids and their derivatives such as methyl esters in single component and internally mixed multicomponent fine mode particles. Initial emphasis was placed on the heterogeneous reaction of oleic acid and ozone gas. Oleic acid was an ideal compound for these nascent studies: it has established reactivity with ozone in solution and as a pure liquid\textsuperscript{1-3}; it is ubiquitous in atmospheric aerosols\textsuperscript{4-9}; it is commercially available in very high purity; and is a liquid at room temperature that can be readily converted into an aerosol by nebulization. The results of the experiments revealed that the ozonolysis of oleic acid showed product formation more akin to liquid phase reactivity rather than to reactions in the gas phase. This is most likely due to the stabilization of the Criegee intermediates that are formed on or near the surface of the ozonized particle, as opposed to gas phase ozonolysis where this intermediate has a predominate decomposition pathway\textsuperscript{10-12}. A host of products associated with the reactivity of stabilized Criegee intermediates were observed including secondary ozonides, geminal diperoxides, and $\alpha$-acyloxyalkyl hydroperoxides. It should be emphasized that these studies with PERCI AMS were amongst the first online aerosol mass spectrometry based measurements of these higher molecular weight ozonolysis products in actual organic aerosol particles. (The emphasis on “actual” in the prior sentence is intentional – there is
a rich tradition in atmospheric chemistry of investigating the oxidation of organic films as proxies for actual particles \(^{13\text{-}16}\); however, these studies usually focus on gas phase product evolution and ozone loss, abnegating detailed chemistry of the condensed organic phase, which was the focus of the PERCI AMS based research presented in this work.)

The detection of polymeric \(\alpha\)-acyloxyalkyl hydroperoxides by PERCI AMS and by other recently developed aerosol mass spectrometric methods\(^ {17\text{-}19}\) was particularly significant since the formation of the class of compounds in oxidized oleic acid has been very recently shown to dramatically enhance CCN activation in ozonized oleic acid particles \(^ {20}\).

The PERCI AMS analysis of the heterogeneous ozonolysis of primary aliphatic amines has several notable features that merit reiteration. The formation of NO\(_2\), NO\(_3\), and nitric acid based clusters proposed to be initiated by the mechanism progressive oxidation in the particulate amines by ozone may help explain the field observation of these gas phase species being formed in particle rich air parcels and hydrometeors, such as fogs \(^ {21\text{-}25}\). Since amines are significant class of compounds observed in both biogenic \(^ {26\text{-}29}\) and anthropogenic \(^ {30\text{-}31}\) emissions the potential role of this reaction in contributing towards NO\(_x\) and NO\(_y\) air pollution merits further investigation. To the best of my knowledge, the reaction of amines with the product(s) of ozonolysis (i.e. stabilized Criegee intermediates and/or secondary ozonides) to give amides, as opposed to classic acylation \(^ {32}\), was described for the first time by PERCI AMS. This may be of significance to source apportionment since amides are typically considered molecular markers for biomass burning events \(^ {33}\) or urban emissions \(^ {34}\) that often have meat cooking aerosols \(^5\text{,}^8\).
as a significant contributor to particulate load – as of late the role of oxidative processing by ozone in forming amides is generally not considered in these apportionments.

In addition to the results presented in Chapters 2 – 5, a summary of other PERCI AMS experiments and of a critical review on the heterogeneous processing are presented as citations with abstracts in Chapter 8.

6.2. Future Directions

This section will place emphasis on experiments featuring PERCI AMS that will build upon the nascent work with organic aerosols presented in this document.

One of the main advancements to PERCI AMS that is needed for future investigations is the ability to monitor the changes in particles of a single radius, i.e. monodisperse aerosols. This would facilitate the application of PERCI AMS to the measurement of the uptake coefficient ($\gamma$) of a reactive trace gas for monodisperse aerosols. In the context of the heterogeneous processing of a particle by a reactive trace gas, the uptake coefficient is a constant relating the flux ($J$) of a trace gas species and the collision rate of the gas with the surface ($n_g \bar{c}/4$)$^{36-38}$:

$$J = \frac{n_g \bar{c} \gamma}{4},$$
where $n_g$ is the density of the gas molecules and $c$ denotes their average thermal speed. Clearly the value of $\gamma$ has to be less than or equal to unity since the flux cannot exceed the collision frequency of the gas with the surface if the particle. Experimentally, the aerosol mass spectrometry research community tries to link the loss of particle phase compound with the uptake coefficient, for example in the oleic acid (OL) + ozone heterogeneous reaction system\textsuperscript{38, 37}:

\[
\frac{d[\text{OL}]}{dt} = \frac{3n_{\text{O}_3} c\gamma}{4a},
\]

where “$a$” is the particle radius and the ratio of 3 to $4a$ accounts for the surface to volume ratio of the spherical particle. Due to the gas-particle interactions $n_{\text{O}_3}$, $a$, and $\gamma$ vary as a function of time such that general analytical solutions of this equation and the flux equation for $J$ are not available\textsuperscript{38, 37}. A model has been developed\textsuperscript{38, 37} that attempts to decouple the uptake coefficient into constituent chemical and physical processes such as gas and particle-phase diffusion, mass accommodation, and adsorption. However, in this model (commonly called the decoupled resistor model\textsuperscript{38, 37}) there are still no general solutions for equations that relate the loss of the condensed phase species with the uptake coefficient, but solutions have been described in several limiting cases. Although the details and formalism of the resistor model are beyond the scope of this work, the
requisite feature in deciding these cases is comparing the particle radius with the diffusoreactive length \((l)^{38,37}\):

\[
l = \left( \frac{D}{k} \right)^{1/2},
\]

where \(D\) is the diffusion coefficient of the reactive trace gas in the reactive matrix and \(k\) is the pseudo-first order rate constant.

As of late, the sensitivity of PERCI AMS to organic components of particles is too low to allow kinetic measurements of monodisperse particulate matter. (At the current level of PERCI AMS sensitivity it requires over 30 minutes of deposition of a monodisperse aerosol of oleic acid (~100-300 nm diameter) to get a signal great enough to do meaningful kinetic studies.) Recently developed aerosol pre-conditioning methods may help overcome this experimental challenge. For example, a recent advancement in the aerosol research community, the versatile aerosol concentration enrichment system (VACES)\(^{39-42}\) is an aerosol pre-conditioning method that, as explained below, if coupled to PERCI AMS may facilitate the ability to study monodisperse aerosols. In a recent study by Geller et al.\(^{39}\) an approximately 19-fold average enrichment of fine mode ambient aerosols was shown by utilizing the VACES method. Similar results have been reported for fine mode particles of ammonium nitrate, ammonium sulfate, and adipic acid\(^{40,41}\). The VACES method achieves fine particle enrichment by initially growing the particles to larger diameters via supersaturation in water vapor; the larger droplets are then concentrated by inertial virtual impaction; and finally the particles are returned to
their initial size by diffusion drying\textsuperscript{42}. While coupling VACES to PERCI AMS could help increase the sensitivity to a monodisperse aerosol beam caution should be taken in generalizing its analytical merit to applicability towards concentrating fatty acid organic aerosols. The low solubility of water in fatty acids may lead to less pronounced particle growth upon exposure to water vapor compared to more water soluble particulate such as nitrate salts\textsuperscript{40, 42}. This may lower the efficiency of particle concentration by inertial virtual impaction and subsequently decrease the enrichment factor. VACES, in its current design, coupled to PERCI AMS would probably greatly benefit kinetic studies of monodisperse fine mode water soluble particles (i.e. ammonium salts, small dicarboxylic acids such as malonic acid) but may be of less applicability to particles rich in organic compounds that have low water solubility.

The results presented in this work focused on the heterogeneous processing of organic aerosols by ozone. As of late, other studies featuring aerosol mass spectrometric methods have also emphasized the chemistry of ozone with organic particles\textsuperscript{17-19, 43-47}. Conversely there is a dearth of studies on the heterogeneous chemistry of arguably the most important gas phase oxidant of the troposphere: the hydroxyl radical (OH). At the time of writing there have been several very recent studies of the heterogeneous oxidation of organic particles by OH\textsuperscript{48-50}, with one study measuring the uptake coefficient ($\gamma_{OH}$) of OH on oleic acid coated sodium chloride particles\textsuperscript{49}. The disparity between the numbers of heterogeneous organic aerosol featuring ozone as the reactive trace gas studies compared to those with OH arises mainly from the relative ease of generating ozone by commercially available sources (usually electric discharge based), and straightforward
quantification by spectrophotometry. There have been some recent improvements in the generation and detection of gas phase OH and they have been mainly applied to the heterogeneous processing of organic films\textsuperscript{15, 51, 52}. For example, OH can be produced by the reaction\textsuperscript{52}:

\[ H + NO_2 \rightarrow OH + NO \]

where atomic hydrogen is generated in a commercially available microwave cavity from He and H\textsubscript{2}. The OH is quantified by chemical ionization mass spectrometry (CIMS) with typical experimental number densities of $0.1-100 \times 10^8$ cm\textsuperscript{-3} \textsuperscript{52} (c.f. typically tropospheric OH levels are \( \sim 10^6 \) cm\textsuperscript{-3}, and nighttime levels are about one order or magnitude lower\textsuperscript{53}). In brief, other methods of OH generation include:

- Generation of OH by the near ultraviolet photolysis of HONO\textsuperscript{49}.
- The near ultraviolet photolysis of ozone to O(\textsuperscript{1}D) and subsequent reaction with water vapor yielding OH\textsuperscript{49}.
- The microwave generation of atomic hydrogen and reaction with O\textsubscript{2} giving the hydroperoxy radical (HO\textsubscript{2}). The HO\textsubscript{2} reacts with H giving OH. \textsuperscript{52}

Besides CIMS most of the other reported methods of quantification of OH concentration are indirect and involve offline analysis \textsuperscript{54, 21, 55, 56} of a hydroxylated product (e.g. phenolic compounds\textsuperscript{55, 56}). These methods require typically require a knowledge of
efficiency of formation of the hydroxylated products and the use of high performance liquid chromatography (HPLC) and ultraviolet-visible detectors.\textsuperscript{55, 56}

The coupling of an OH generating and detection system to PERCI AMS for preliminary investigations of the heterogeneous processing of organic aerosols by this ubiquitous tropospheric oxidant would benefit the atmospheric research community in several regards. These studies would help answer the question of whether the oxidation of organic particulates by OH is in accord with gas or liquid phase reactivity trends. Secondly, physical changes in the particulate, such as an increase in the oxygen to carbon ratio as a result of oxidative processing by OH or other free radical could increase the water solubility\textsuperscript{57, 58} of the particle and subsequently increasing its CCN activity\textsuperscript{57-60}. The potential complexity of the reactivity OH and other gas phase free radicals with organic particles is likely to be comparable to the results presented in the recent study by Hearn et al.\textsuperscript{61} with the oxidation of dioctyl sebacate particles with the chlorine radical in O\textsubscript{2}. In this study the high yield of ketone products relative to alcohols is indicative of the Russell mechanism\textsuperscript{62, 63} (i.e. 2 RO\textsubscript{2} \rightarrow ketone + alcohol + O\textsubscript{2}), which is a radical reaction in condensed phases\textsuperscript{61-63}. However, as noted by Hearn et al.\textsuperscript{61} there was evidence of “marked dependence” of the ketone yield on the molecular oxygen concentration. This suggested the reaction of alkoxy radicals with molecular oxygen forming ketones (i.e. RO + O\textsubscript{2} \rightarrow HO\textsubscript{2} + ketones)\textsuperscript{61} which is commonly associated with gas phase oxidation\textsuperscript{64}. A very recent report by George et al.\textsuperscript{48} on the heterogeneous reaction system of gas phase OH and DOS particles has similar findings to those of Hearn et al.\textsuperscript{61}, namely evidence of both hydroxyl chemistry commonly associated with liquid and gas phase reactivity. It is
important to note that in both of these studies there was a marked increase in density of the DOS particles, inferring an increase in the oxygen to carbon ratio, and secondly that esters such as DOS have been shown to be non-reactive towards ozone$^{19, 65, 66}$. These preliminary results indicate that common tropospheric free radical gas phase oxidants (i.e. OH, Cl) are probably important in the aging of organic particulate matter and may have a role in CCN activation of these particles. PERCl AMS experiments investigating the heterogeneous reactivity of single and multicomponent organic aerosols with OH and other free radical gas phase oxidants would likely contribute to developing a better overall description of atmospheric aging of the organic aerosols.

6.3. References


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8. Additional Citations with Abstracts

The following citations and abstracts are for material that was not directly included in this dissertation but was part of my research at the University of Vermont. The first two of citations and abstracts correspond to experimental work; the last citation and abstract corresponds to a critical review.


Photoelectron resonance capture ionization (PERCI) mass spectrometry has been developed for the direct online analysis of organics, including lipids. Analysis is conducted without the need for sample preparation or chemical derivatization such as methylation, foregoing the use of harmful or toxic chemicals. PERCI is currently being adapted towards the analysis of edible oils. Herein, as a proof of principle of the simplicity and potential utility of this method towards the analysis of edible oils, we present the analysis of the prevalent fatty acids (FA) in Tuscan extra-virgin olive oil along with triolein and linolenic acid (LNA) standards. Ionization of olive oil results in little fragmentation of the prevalent FA, which are measured as their molecular ions, [FA–H]. The relative concentrations of these FA determined by PERCI were in good
agreement with established values. Further utility of PERCI was demonstrated by interrogation of ozonized LNA and olive oil, with 13 of the 18 anticipated products of the ozonolysis of LNA measured as their molecular anions, [M–H]. Similarly, the PERCI mass spectrum of ozonized olive oil showed all the anticipated ions of the predominant FA, oleic acid, as well as many molecular ions arising from less abundant unsaturated FA.


Photoelectron resonance capture ionization aerosol mass spectrometry (PERCI-AMS) has been applied to the analysis of proxies for marine aerosols with and without ozone; proxies used were mixed oleic acid–amino acid particles. The mechanism of ion formation for serine (104m/z), glutamic acid (146m/z), and phenylalanine (164m/z) was dissociative electron attachment. This corresponds to loss of the hydrogen atom only, allowing for straightforward identification of the free amino acids. No ozonolysis products for the free amino acids were observed, even at high concentrations of ozone (500 ppm for 19 s). The direct detection of a novel gas-phase hydrated anion, [serine-H$_2$O–H], is described. These preliminary results suggest that PERCI-AMS may provide an effective, simple and direct online method for the detection of organic nitrogen from free amino acids for future field studies of the marine troposphere.

The heterogeneous processing of organic aerosols by trace oxidants has many implications to atmospheric chemistry and climate regulation. This review covers a model heterogeneous reaction system (HRS): the oleic acid-ozone HRS and other reaction systems featuring fatty acids, and their derivatives. The analysis of the commonly observed aldehyde and organic acid products of ozonolysis (azelaic acid, nonanoic acid, 9-oxononanoic acid, nonanal) is described. The relative product yields are noted and explained by the observation of secondary chemical reactions. The secondary reaction products arising from reactive Criegee intermediates are mainly peroxidic, notably secondary ozonides and $\alpha$-acyloxyalkyl hydroperoxide oligomers and polymers, and their formation is in accord with solution and liquid-phase ozonolysis. These highly oxygenated products are of low volatility and hydrophilic which may enhance the ability of particles to act as cloud condensation nuclei (CCN). The kinetic description of this HRS is critically reviewed. Most kinetic studies suggest this oxidative processing is either a near surface reaction that is limited by the diffusion of ozone or a surface based reaction. Internally mixed particles and coatings represent the next stage in the
progression towards more realistic proxies of tropospheric organic aerosols and a
description of the products and the kinetics resulting from the ozonolysis of these proxies,
which are based on fatty acids or their derivatives, is presented. Finally, the main
atmospheric implications of oxidative processing of particulate containing fatty acids are
presented. These implications include the extended lifetime of unsaturated species in the
troposphere facilitated by the presence of solids, semi-solids or viscous phases, and an
enhanced rate of ozone uptake by particulate unsaturates compared to corresponding gas-
phase organics. Ozonolysis of oleic acid enhances its CCN activity, which implies that
oxidatively processed particulate may contribute to indirect forcing of radiation.